

FINAL REPORT

A Survey of the Water Quality of Streams in the Primary Region of Mountaintop / Valley Fill Coal Mining

October 1999 to January 2001

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Mountaintop Mining / Valley Fill
Programmatic Environmental Impact Assessment

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1. SUMMARY

1.1 Background

The Project Plan was designed to characterize and compare impacts to stream chemistry from mountaintop mines and associated valley fills (MTM/VF). This study used the same 37 stream monitoring sites used in the aquatic biology study of this same region. Most sites were visited, sampled, and had flow rate measured 13 times between October 1999 and February 2001 by field crews who are Mine Inspectors for the state of West Virginia. Four field parameters and 37 laboratory parameters were selected to be monitored at each site. Ten of those parameters had stream water quality criteria limits which were used to set measurement detection limits. One set of duplicate samples and two blank samples were to be collected each day by each field crew to enable assessment of sampling errors and sampling precision. The field work exceeded the goal of 90% completeness for site visits, stream sampling, flow measurements, and duplicate samples, but only 83 % of the number of blank samples were collected.

The contract for chemistry analyses was changed to a second laboratory in July 2000. EPA Region III chemists provided a QA/QC review of the laboratory data. Only 83 % of the values reported by the first laboratory passed the QA/QC review. The second laboratory had 98% of their data pass the QA/QC review. Corrective actions were implemented during the study to resolve problems in the field and laboratory. The data from this study is stored in a relational database which is part of this report.

1.2 Evaluation of Results

The results were evaluated and are presented under three lines of reasoning: 1) parameters altered by MTM/VF mining; 2) parameters violating stream water quality standards; 3) parameters not detected in any sample. Parameters likely to be impacted by MTM/VF mining were identified and used as an outline for evaluating the entire database from all categories of sites. Variations in data quality were assessed using the results of the duplicate samples and blank samples. Additional characterization of the categories of sites is provided by calculation of "Yield" rates, an idea taken from a USGS publication.

The data indicate that MTM/VF mining activities increase concentrations of the several parameters in streams. Sites in the category Filled had increased concentrations of the following parameters: sulfate, total calcium, total magnesium, hardness, total dissolved solids, total manganese, dissolved manganese, specific conductance, total selenium, alkalinity, total potassium, acidity, and nitrate/nitrite. There were increased levels of sodium at sites in the category Filled/Residences which may be caused by road salt and/or sodium hydroxide treatment of mine discharges.

The data were inconclusive for several other parameters which were detected in only a few

samples or at very low concentrations. Those parameters: total phosphorous, total copper, total lead, total nickel, total barium, total zinc, total organic carbon, dissolved organic carbon, and total suspended solids. Other parameters were detected but there was no clear indication of stream impacts resulting from MTM/VF mining operations. Those parameters are: chloride, total aluminum, dissolved aluminum, total iron, dissolved iron, temperature, dissolved oxygen, and pH. Data from the second laboratory indicated that only three samples for total aluminum exceeded the stream criterion and all were collected August 9, 2000 at sites with fills upstream. Dissolved aluminum was detected in only five samples and all were near the detection limit of 100 ug/L. There were no samples for total iron exceeding the stream criterion but several samples in the category Filled approached the limit in the fall of 2000. Dissolved iron was detected at a few sites in the category Filled at levels slightly higher than other sites. MTM/VF mining operations can increase iron concentrations in streams but there is no clear evidence that this occurred during the study. Temperature, pH, conductivity, and dissolved oxygen were measured in the field. The only field parameter clearly impacted by MTM/VF mining was conductivity which was noticeably increased at sites in the category Filled.

Parameters which were not detected in any sample analyzed at the second laboratory were: total arsenic, total antimony, total cadmium, total chromium, total cobalt, total vanadium, total thallium, total beryllium, total mercury, and total silver. Hot acidity was analyzed for a few samples and none was detected.

Only the data from the second half of the study was used to evaluate compliance with stream limits due to problems with contamination in blanks, excessive holding times and less precision which occurred during the first part of this study. The latter data indicate that MTM/VF mining is associated with violations of the stream water quality criteria for total selenium. Selenium violations were detected in each of the five study watersheds and all were at sites in the category Filled, downstream of MTM/VF operations. No other site categories had violations of the selenium limit. There were no violations of the limits for total beryllium, chloride, total mercury, total silver, temperature. The data do not support a conclusion regarding stream water quality violations for aluminum, dissolved oxygen, iron and pH which can be impacted by MTM/VF mining activities.

While outside the scope of this report, there would be value in having experts evaluate the flow rate data from this study to identify impacts attributable to mining. Base flows of streams with valley fills are reported to be 6 to 7 times greater than the base flows of unmined areas. During base flow conditions, the more highly mineralized water from fills becomes a larger portion of stream flow, altering the stream water chemistry.

2. STUDY OBJECTIVES

The final Project Plan for this study listed two objectives:

- Characterize and compare conditions in three categories of streams:
 - 1) streams that are not mined;
 - 2) streams in mined areas with valley fills; and
 - 3) streams in mined areas without valley fills.
- Characterize conditions and describe any cumulative impacts that can be detected in streams downstream of multiple fills.

This study was designed to supplement other studies of stream water quality impacts resulting from mountaintop mining and valley fill (MTM/VF) coal mining operations. This study compliments the aquatic biology study for this same region by gathering chemistry data on the same stream sites used by USEPA Biologists in their evaluation of MTM/VF impacts to aquatic organisms. The aquatic biology study report by Green, Passmore, and Childers is titled A Survey of the Condition of Streams in the Primary Region of Mountaintop Mining/Valley Fill Coal Mining. A separate report is being prepared to evaluate the relationships between the chemical data and biological data.

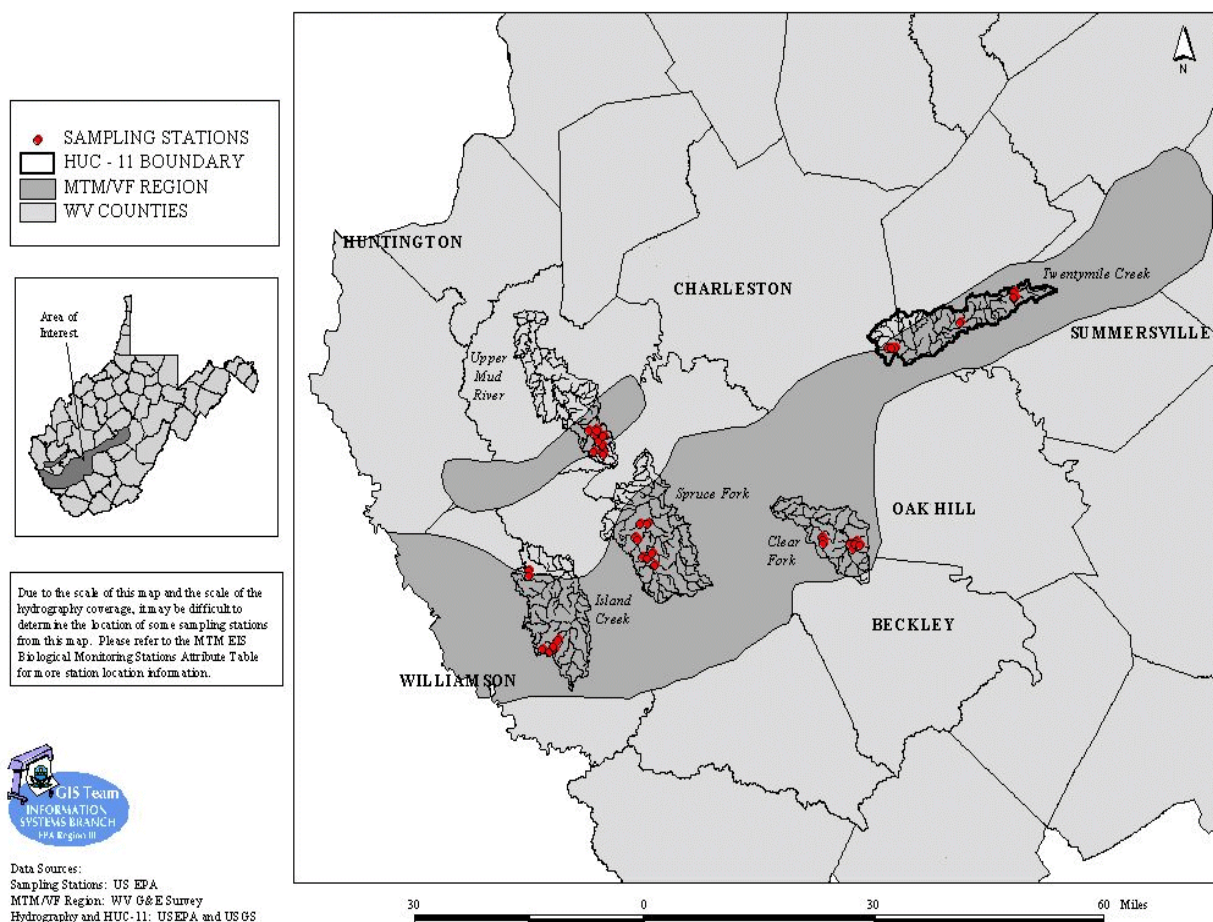
3. THE PROJECT PLAN

A Project Plan was drafted for this study in the summer of 1999 under the direction of the Environmental Impact Statement Steering Committee. The plan was posted on EPA Region III's web site. The plan was revised several times as the study progressed in response to comments and problems encountered during the study.

3.1 Monitoring Sites Description

The thirty seven (37) stream monitoring sites are exactly the same sites used by the USEPA Biologists in their study of MTM/VF. They provide a synoptic survey of stream conditions in five watersheds across the primary MTM/VF region in West Virginia. These watersheds are Twentymile Creek, Clear Fork, Island Creek, upper Mud River and Spruce Fork. The locations of the sites are shown in Figure 1. They are spread across the region of mountaintop mining in West Virginia. The sites were selected with the experienced assistance of WVDEP Mine Inspectors familiar with mining activities in the region and with the cooperation of coal companies in the area.

SAMPLING WITHIN THE REGION OF MAJOR MOUNTAINTOP REMOVAL MINING ACTIVITY IN WEST VIRGINIA



EPA R3 GIS TEAM PROJECT SIG541 H. CHILDERS 09/19/00 MAP# 1029

FIGURE 1. Map of Stream Sampling Site Locations

The distribution of sites within the three categories identified in the study objectives are:

1) streams that are not mined - Unmined -	9 sites
2) streams in mined areas with valley fills -	21 sites
(Filled 15sites + Filled/Residences 6 sites)	
3) streams in mined areas without valley fills -	6 sites
(Mined 4 sites + Mined/Residences 2 sites)	
Flow diversion ditch at a valley fill -	1 site
TOTAL	37 sites

The site numbers and descriptions are listed in Table 1. The station numbers are not sequential since the 37 biological sampling sites were chosen from 127 possible sampling sites. The sizes of the drainage areas upstream of the sites vary from 125 acres to 27,742 acres. Only three of the 37 sites have watersheds larger than 3,200 acres.

TABLE 1
Monitoring Site Attributes

Site Identification	EIS Class	Watershed	Area (acres)	No. of Fills	Comment/ Permit Date	No. of Visits	No. of Samples	No. of Flowrates
MT-01	Mined/Residence	upper Mud River	1,897		Past Logging	13	13	12
MT-02	Unmined	upper Mud River	511		Past Logging	13	13	12
MT-03	Unmined	upper Mud River	717		Past Logging	13	13	12
MT-13	Unmined	upper Mud River	335		Past Logging	13	12	12
MT-14	Filled	upper Mud River	1,527	8	'85,'88,'89	13	13	12
MT-15	Filled	upper Mud River	1,114	6	'88,'89,'91,'92,'95	13	13	12
MT-18	Filled	upper Mud River	479	2	'92,'95	13	13	13
MT-23	Filled/Residence	upper Mud River	10,618	26	'85,'88,'89,'91,'92,'95,'96	13	13	12
MT-24	Ditch	upper Mud River	N/A	1	'88,'91	13	13	13
MT-25B	Filled	Spruce Fork	997	1	'86	13	13	13
MT-32	Filled	Spruce Fork	2,878	5	'86,'88,'89,'91	13	13	13
MT-34B	Filled	Spruce Fork	1,677		'85,'86	13	13	13
MT-39	Unmined	Spruce Fork	669			13	13	13
MT-40	Filled/Residence	Spruce Fork	11,955	10	7 VF + 3 refuse	13	13	13
MT-42	Unmined	Spruce Fork	447			13	13	12
MT-45	Mined	Spruce Fork	1,111		'87 strip @ head	13	13	13
MT-48	Filled/Residence	Spruce Fork	27,742	22	4 communities	13	13	13
MT-50	Unmined	Island Creek	563			13	13	12
MT-51	Unmined	Island Creek	1,172		gas well	13	11	10
MT-52	Filled	Island Creek	316	1	underground entry & fill / '84	13	13	13
MT-55	Filled/Residence	Island Creek	3,167	5	'86,'88,'89,'93,'94,'98	13	13	12
MT-57B	Filled	Island Creek	125	1	'88	12	12	11
MT-60	Filled	Island Creek	790	2	'88,'93	13	13	12
MT-62	Filled/Residence	Clear Fork	3,193	11	'89,'91,'92	14	14	14
MT-64	Filled	Clear Fork	758	5	'92,'93	14	14	14
MT-69	Mined/Residence	Clear Fork	708		pre- '65	14	14	14
MT-75	Filled/Residence	Clear Fork	876	5	'89,'92	14	14	14
MT-78	Mined	Clear Fork	524		pre- '65	14	2	2
MT-79	Mined	Clear Fork	448			14	14	14
MT-81	Mined	Clear Fork	1258		NaOH / pre '65	14	14	14
MT-86	Filled	Twentymile Creek	2,201	3	NaOH/ '90,'93	14	14	14
MT-87	Filled	Twentymile Creek	752	3	NaOH/'90,'93	14	14	14

MT-91	Unmined	Twentymile Creek	1,302		haul road	14	14	14
MT-95	Unmined	Twentymile Creek	968		logging?	14	14	14
MT-98	Filled	Twentymile Creek	1,208	8	'77,'82,'90	14	14	14
MT-103	Filled	Twentymile Creek	1,027	6	'77,'82,'90	14	14	13
MT-104	Filled	Twentymile Creek	2,455	8	'77,'82,'90	14	14	14
Totals	37 sites					494	479	466

3.2 Monitoring Frequency

Stream samples were collected during the period of October 1999 thru February 2001. The sites were to be sampled monthly but the scheduling of when samples were taken was determined by availability of the field crews. The stream sampling effort was stopped in May 2000 due to problems with timely delivery of chemistry laboratory data. A contract was completed with a different laboratory and monthly sampling resumed in August 2000 and continued through February 2001. Most sites were visited 13 times for sampling. One field crew took an additional set of samples from the seven sites in Twentymile Creek in November 1999 and another crew took an additional set of sample from the seven sites in Clear Fork in June of 2000. A few times, some of the sites had no flow to sample. The field crew found stream flow on only two occasions at site MT-78. There were 479 stream samples collected in this survey, not counting the duplicates and other QA samples. Flow measurements were also made during sampling but there were several occasions when flows were not measured. This was especially true during winter months when the stream was frozen over. There were 467 flow measurements for this study. Table 1 lists this information for each sample site.

3.3 Monitoring Parameters and Sampling Methods

The parameters to be monitored were discussed by numerous groups and experts. The list of parameters finally selected was shaped by constraints of holding times, detection limits, difficulty in sampling and other factors. The discussion on what parameters to monitor began with a review the stream water quality parameters for the streams in the study area.

3.3.a Stream Water Quality Criteria

There are limits set on the concentrations of chemicals allowed in streams across the nation. Each State has established these stream water quality criteria for the surface waters of their State. West Virginia has three categories of stream water quality criteria set to protect specific water uses. Those categories of water uses are: 1) Aquatic Life, 2) Human Health, and 3) All Other Uses. The Aquatic Life Criteria are the limits most applicable to this study because those are designed to protect aquatic life in the stream. There can be separate limits for warm water and cold water (trout) streams. Sometimes there are also separate limits for acute and chronic exposure. Acute exposures would be those experienced during a short time period such as a spill. Chronic limits are usually lower than Acute limits since the organisms are exposed for a

longer time period. Water quality criteria also vary with sample methods. Some criteria specify “Not to exceed” which is a grab sample of the stream. These criteria are applicable to the sampling methods used in this study. There are also some criteria set for a “one-hour average” which are not strictly applicable to the single grab sample results of this study, but they are still valuable in evaluating if there are concerns about the concentrations of chemicals identified in this study. The West Virginia Water Quality Criteria limits are discussed in Attachment 1.

3.3.b Mining Permit Monitoring

Coal companies seeking permits must monitor streams above and below their proposed mining sites as part of the process for getting a mining permit. It was agreed that the list of parameters being monitored for permits would be expanded to include the parameters being monitored in this study. Discussions with coal companies were held to invite their comments on the list of parameters. This list of “interim protocol” parameters was adopted for coal companies seeking permits in West Virginia. They were asked to monitor for the list of “interim protocol” parameters as part of their pre-mining data gathering effort. The data gathered by the coal companies and their consultants could also be used to in evaluating the impacts of mining but that data has not been included in this report. A separate report is being prepared using coal company data for this EIS effort.

3.3.c Laboratory Parameters

After much discussion and evaluation, the 37 chemical parameters listed below were selected for laboratory analyses. The samples were to be collected and preserved and analyzed following procedures consistent with 40 CFR Part 136.

Water Quality (10)

Acidity	Nitrate + Nitrite	Total Organic Carbon
Alkalinity	Sulfate	Dissolved Organic Carbon
Chloride	Total Suspended Solids	
Hardness	Total Dissolved Solids	

Total Metals (27)

Aluminum	Cobalt	Nickel
Dissolved Aluminum	Copper	Potassium
Antimony	Iron	Phosphorous
Arsenic	Dissolved Iron	Selenium
Barium	Lead	Silver
Beryllium	Magnesium	Sodium
Cadmium	Manganese	Thallium
Calcium	Dissolved Manganese	Vanadium
Chromium	Mercury	Zinc

Hot acidity was also analyzed for a brief period by the second laboratory by mistake.

3.3.d Field Parameters

Field crews were WVDEP Mine Inspectors. They were briefed in the standard monitoring procedures at the start of this study. The briefing included instructions in measuring Dissolved Oxygen, Specific Conductivity, Temperature, and pH *in situ* using calibrated electrometric field meters. The field chemistry measurements taken at each sampling site were consistent with 40 CFR Part 136. The field crew recorded measurements and other sample site information on field sheets which were sent to the lab with the samples. They also measured flow rate at the time of sampling using methods suitable for effluent discharge monitoring under the NPDES program. EPA office staff used a computer program to calculate stream flows from the field stream gaging data. A copy of the blank field sheets used in this study is included as ATTACHMENT 2.

3.4 Stream Sample Collection and Shipping

The laboratory provided sample containers, chemical preservatives, lab-pure water, labels, and shipping containers. They were shipped to the WVDEP field offices. The sampling procedures used were consistent with the 40 CFR Part 136 and samples were collected as grab samples in mid-stream. The samples were preserved and stored on ice in the shipping containers until they were ready to ship to the lab following chain-of-custody procedures. A separate field sheet for each sample, as shown in Attachment 2, was to be placed in the shipping containers.

3.5 Methods and Detection Limits for Water Quality Criteria Parameters

Ten of the parameters monitored during this study have an applicable stream water quality criteria. These criteria were used to select methods of analysis and detection limits for the laboratory analyses. The concern was that values reported by the laboratory as exceeding the stream criteria would be measured precisely enough to confidently say that stream criteria were exceeded. Therefore the detection limit or lowest measurable concentration reported by the laboratory was arbitrarily designated to be no greater than one third of the lowest applicable water quality criterion. The detection limit for this study was set after discussions with chemists as to what detection limits are achievable following excellent laboratory practices. The method selected and the detection limit for each parameter with a criterion are included in Table 2.

TABLE 2
Water Quality Criteria and Method Detection Limits

<i><u>Parameter</u></i>	<i><u>Water Quality Criterion</u></i>	<i><u>Method</u></i>	<i><u>Detection Limit</u></i>
Total Aluminum	750 ug/L	EPA 200.7	100 ug/L
Total Beryllium	130 ug/L	EPA 200.7	1 ug/L
Chloride	230 mg/L	EPA 300.0	5.0 mg/L
Dissolved Oxygen*	5.0 mg/L	Field Meter	0.1 mg/L
Total Iron	1.5 mg/L	EPA 200.7	0.10 mg/L
Total Mercury	2.4 ug/L	EPA 245.1	0.2 ug/L
pH*	6.0 to 9.0	Field Meter	0.1 pH unit
Total Selenium	5 ug/L	EPA 200.8	3 ug/L**
Total Silver	1 to 43 ug/L	EPA 200.7	10 ug/L
Temperature*	73 ^o or 87 ^o F	Field Meter	+/- 2 ^o F

* Field meter required to measure these parameters.

** The estimated instrument detection limit for selenium in water using Method 200.8 (Inductively Coupled Plasma - Mass Spectrometry) is around 5 ug/L according to the 1983 EPA Methods Manual.

4. DATA QUALITY REQUIREMENTS AND ASSESSMENTS

4.1 Field Work

The field work was conducted by personnel from the West Virginia Division of Environmental Protection, Office of Mining & Reclamation and reviewed by the EPA staff.

4.1.a Field Work Completeness Assessment

The project plan requires a monthly visit to each site, a sample from each site when there is flow, and a flow measurement. The field data are recorded on field sheets for each sample. The field crews sent copies of their field sheets to the EPA as well as to the contract labs with the samples. The EPA monitored the progress of the field work by reviewing and evaluating these field sheets. Some crews also reported problems and progress through telephone conversations with the EPA.

The data and notes from the field sheets was transferred to the electronic database by the EPA staff. All flow rates were calculated from the field readings by laboratory personnel or EPA staff using the same computer program. The electronic records were then completely checked for data entry errors. These records were then used to cross check the records and data received from the laboratories and the QA/QC review. The calibration records for field meters were not included in the electronic database of data for this study, but the comments from the field sheets are included.

4.1.b Field Work Sampling Errors Assessment

The Project Plan specified three types of QA samples be collected by each crew each day of sampling. **Field Duplicate Samples** were collected as two identical sets of stream samples from a stream monitoring site. The second set was labeled as a Duplicate Sample. The concentrations of each parameter in these pairs of Duplicate Samples should be nearly identical. **Blank Samples** were collected in a set of sample containers using lab-pure water from the laboratory and preserving them just like the stream samples, including filtering. These samples were called Blanks and the concentration of all parameters in each sample should be at or near the detection limit. The third type of QA sample used in this survey was a **Trip Blank Sample**. This was a set of sample containers filled with lab-pure water in the laboratory and sent to the field crews with the other sample containers and preservatives. This Trip Blank was opened in the field at the sample site and preserved as the stream samples, except there was no water filtered in the field in the Trip Blank. Any measurable concentrations parameters in these blank samples would indicate concerns with sample handling or contaminated sampling equipment. QA samples were tested in the laboratory for the same parameters as the stream samples. Although the QA samples were collected to evaluate problems with sample collection and handling in the field, they can also be used to detect errors in measurement which occur in the laboratory.

4.1.c Field Duplicates

Field Duplicate data can be used to calculate an estimate the precision of sampling methods. This estimate of precision includes error associated with field collections at the site, error in sample handling, and error associated with laboratory activities as well as true variation in the water being sampled. Since it is not possible to separate the variation caused by sampling error or sample handling error from the variation caused by measurement error, the differences between sets of duplicate samples can only give an estimation of precision in sampling. The estimate of precision in this study is based on laboratory results of Field Duplicate samples. Field Duplicate samples were to be collected at 10% of the sites on each sampling occasion (one Field Duplicate per sampling crew per day). Only the first of the two sets of sample results was used in calculating and evaluating the monitoring trends and statistics for a site.

Precision estimates were calculated from the data for Field Duplicate samples using **Relative Percent Difference (RPD)**. RPD is calculated using the following equation:

$$RPD = ((C_1 - C_2) \times 100) \div ((C_1 + C_2) / 2)$$

where: C_1 = the larger of the two values and
 C_2 = the smaller of the two values.

Often the smaller of the two values was below the minimum concentration the laboratory could detect (called the Detection Limit or DL). In calculating statistics on the concentration at a site, every time a reported value was below the DL, a value of one half the DL was assigned as the

smaller value (C_2), rather than zero. The RPD varies with each parameter and for each set of duplicates. There are tables of RPD results for selected parameters in this report under the section Evaluation and Discussion of Results. As the concentrations in the duplicate samples approach the detection limit, the RPD values are not as meaningful an estimate of precision. There is a trend in the data from this study for the RPD to improve (get much lower) with later samples. This may be due to improvements in sample collection and handling in the field and laboratory or due to differences between the laboratories.

There is also a trend in the results from this study for the concentrations to be lower in the second half of the study. This may be due to lingering effects of the drought conditions experienced just before the beginning of the sampling in 1999. It could also result from improvements in sample collection and handling in the field and laboratory as the study progressed. It could also be due to differences between the two laboratories. There were detectable concentrations of arsenic, cadmium, lead, manganese, silver and thallium in results from the first laboratory but the second laboratory found no detectable concentrations of these metals in any samples. The first laboratory also reported generally higher concentrations of antimony and nickel than the second laboratory.

Another way to evaluate precision is to **plot concentration of duplicate samples**. The X-axis is the concentration of the first sample and the Y-axis is the concentration of second sample. A point is plotted for each set of duplicate samples. If the values for all sets of duplicate samples are equal, they will make a straight line from the detection limit to the maximum value detected. This approach can be used on duplicate samples of stream samples as well as the duplicate sets of blank samples.

It is recognized that even the best laboratories can not “hit a bulls eye” every time with analytical tests so the study plan allows for a general “precision limit” of plus or minus 25%. The precision limits can also be plotted on the graph of duplicate sample results to illustrate when values of duplicate samples are “out of control” or beyond the precision limit. Graphs of duplicate sample results have been plotted for various parameters using a unique symbol for each laboratory. Errors in sample collection or handling in the field may cause duplicate samples to be “out of control,” but the problem may also be in the laboratory. The plots of duplicate sample results also indicate the precision of the sampling at the second laboratory was much better than the first. This may be due to improvements with experience in collecting and handling samples in the field or it may be related to the laboratory. The end result is that there is more confidence in the precision of sample data from the later portion of the study. There were twice as many duplicate samples analyzed at the second laboratory and the sites were more varied with fewer Unmined sites. As a result the range of concentrations in duplicates is generally wider than at the first laboratory.

4.1.d Blanks

Field crews were to collect two blanks each day they sampled. Not all field crews were equally diligent in collecting and identifying Blank Samples. Problems were identified with each crew not always having the supply of lab pure water and adequate sample containers when they needed them. There were also other communication problems. There were intermittent problems with unacceptable concentrations of contaminants in the blank samples. Some problems were thought to have been caused by field errors such as putting the acid preservatives in the wrong bottle, but this was not confirmed. There was also an intermittent problem with inadequate supplies of lab pure water for blanks and at least one crew noted they purchased distilled water on two occasions to use in the blanks. The quality of the blank water was sometimes questioned by chemists running the samples. The data for all Field Blank samples has been evaluated as a group to identify variability among the parameters. The number of Field Blank samples with detectable concentrations of contamination for each laboratory are listed by parameter in Table 3.

Within the group of blank samples there were 28 pairs of duplicate blanks. These were duplicates for all parameters except those which were filtered in the field. The graph plots of these “duplicate blanks” for selected parameters are included in this report under the section Evaluation and Discussion of Results. The precision and amount of contamination revealed in these graphs indicates that the contamination of blanks decreased in data from the second laboratory. This could be due to improvements in sample handling in the field or in the laboratory. The end result is that there is less contamination of blank samples during the later portion of the study, and there are several parameters which have unreliable results from the first laboratory. The parameters with unreliable results from the first half of this study included acidity, alkalinity, antimony, arsenic, lead, phosphorous, potassium, selenium, thallium, and most critically both suspended and dissolved solids.

The Project Plan calls for sample results from a site to be “flagged” when the concentration of a parameter in the blank (field or laboratory blank) exceeds 1/10th of the value reported in the stream sample. The electronic spreadsheet of the data included as ATTACHMENT 3 has a column identifying all “flagged” data. The code letter “B” identifies results with problems with the excessive contamination in the blank samples.

TABLE 3
Contamination Detected in Blanks

PARAMETER	LAB 1 Number From 30 Samples Greater Than Detection Limit	LAB 2 Number From 50 Samples Greater Than Detection Limit
ACIDITY	28	0
ACIDITY HOT		0*
ALKALINITY	28	0
ALUMINUM, DISSOLVED	4	1
ALUMINUM, TOTAL	3	3
ANTIMONY, TOTAL	24	0
ARSENIC, TOTAL	25	0
BARIUM, TOTAL		0
BERYLLIUM, TOTAL	0	0
CADMIUM, TOTAL	0	0
CALCIUM, TOTAL	13	0
CHLORIDE	5	0
CHROMIUM, TOTAL	8	0
COBALT, TOTAL		0
COPPER, TOTAL	3	2
DISSOLVED, ORGANIC CARBON	3	4
IRON, DISSOLVED	1	0
IRON, TOTAL	4	1
LEAD, TOTAL	24	1
MAGNESIUM, TOTAL	8	0
MANGANESE, DISSOLVED	1	0
MANGANESE, TOTAL	3	1
MERCURY, TOTAL	0	1
NICKEL, TOTAL	12	0
NITRATE	5*	0*
NITRITE	0*	0*
NITRATE+NITRITE	0*	0*
PHOSPHORUS, TOTAL	22	0
POTASSIUM, TOTAL	28	0
SELENIUM, TOTAL	21	1
SILVER, TOTAL	0	0
SODIUM, TOTAL	15	0
SULFATE	1	0
THALLIUM, TOTAL	20	0
TOTAL DISSOLVED SOLIDS	27	1
TOTAL ORGANIC CARBON	3	2
TOTAL SUSPENDED SOLIDS	26	0
VANADIUM, TOTAL		0
ZINC, TOTAL	11	9

* The number of Blank samples for these parameters is less than for other parameters.

4.1.e Field Work Completeness Evaluation

Completeness is a quality assurance/quality control term and is defined as the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Completeness was measured by calculating what percentage of samples were collected and analyzed with valid results. The goal for this project was 90% completeness. Completeness is calculated according to the following equation.

$$C = 100 \times (V/N)$$

where: C = percent completeness

V = number of measurements judged valid

N = total number of measurements.

The percent completeness was calculated for the field work and is presented in Table 4.

TABLE 4
Field Work Data Summary

Factor Being Measured	Numbers (V and N)	Percent Completeness
Attempted Visits to Sites	495 of 495	100
Actual Visits to Sites	494 of 495 Attempts	99.8
Number of Times Sites Dry @ Visit	15	N/A
Number of Samples at Sites	479* of 494 Visits	97.0
Number of Flow Measurements	466 of 479 Samples	97.3
Number of Duplicate Sample Sets	44 of 479 Samples	9.18% / 10% Goal = 91.8%
Number of Blank Samples	80 of 479 Samples	16.7% / 20% Goal = 83.5%

*Excluding the Duplicate and Blank samples.

The field work was especially complete in this study. There was only one occasion during this entire survey when a field crew could not reach a site. A tree had fallen and blocked the road to site MT-57B on September 28, 2000. The percent completeness is 494 visits out of 495 attempts or 99.8 %. This was excellent and greatly exceeded the goal of 90% completeness.

Samples were collected at all sites on every visit unless the streams were dry. Site MT-78 was dry 12 times in this study. In the entire study, there were only 15 site visits which found no stream flow. There were 479 stream samples collected in this survey, not counting duplicates and other QA samples. The percent completeness is 479 samples out of 494 visits or 97.0 %. This was excellent.

Flow rate was to be measured on each sampling occasion. The crews were generally able to measure flows with each round of sampling. However, when they made the sample runs in January of 2001 they found 12 stream sites were covered with ice and stream flows were not measured. The total number of missed flow measurements in this study was only 13. The percent completeness is 466 flows out of 479 samples or 97.3 %. This was also an excellent effort from the field crews.

The goal for field duplicate samples listed in the project plan was to have duplicate analyses performed on 10% of the sites on each sampling occasion. Field crews did not collect any duplicate samples until March 2000 due to several problems with supplying an adequate number of sample containers as well as confusion. From March 2000 on, the crews sampled duplicates as in the work plan. There were 44 duplicates for 479 samples so overall the study performed duplicate analyses on 9.18 % of the sites sampled.

The work plan did not list a numeric goal for the collection of blank samples but the ideal number of blanks should have been 20% of the number of samples. Field crews did not all collect blank samples the same way nor on each sampling day for several reasons. There was an intermittent problem with inadequate supplies of extra sample bottles and lab pure water. There were also communication problems which continued until the end of the study. Some crews collected two sets of blank samples each sampling day calling one set the Field Blank and the other set the Trip Blank. There were 28 pairs of blank samples (56 samples) collected during this study. There were 23 solitary blank samples collected and one day when three blank samples were collected by one crew. There were a total of 80 blank samples collected during the study for 479 samples for a percentage ratio of 16.7%. This falls short of the goal. Although the number of blank samples was high, they were not collected as planned and the differences between crews did not get resolved during the study.

4.2 Laboratory Work

The chemistry analyses of the samples were performed by contractor laboratories. The first lab appeared to be unable to keep up with the work load. Samples were not analyzed within allowable holding times and there were unacceptable delays in submitting laboratory reports and records. In July 2000, a second contract laboratory took over the chemistry analytical work and continued to the end of the study.

EPA Region III's Office of Analytical Services and Quality Assurance (OASQA) developed the plans for doing the QA/QC review of the laboratory data. The data validation process was consistent with those listed in the *"Innovative Approaches for Validation of Organic and Inorganic Data-SOPs"*, June 1995, Section IM-1, entitled: *"Validation of Target Analyte List Metals and Cyanide Data, Manual Approach IM-1."* The review process was designed using experience from the QA/QC procedures that EPA uses in overseeing the Contract Laboratory Program (CLP). The plan was modified when the contract was developed for the second laboratory to focus on a thorough review of 10% of the data. All data from sites MT-03, MT-15, MT-24, and MT32 for the following ten analytes were recalculated by EPA chemists: Sulfate,

(NO₂+NO₃)-N, TOC, DOC, Total Iron, Total Aluminum, Total Manganese, Dissolved Iron, Dissolved Aluminum, Dissolved Manganese. They continued to review the reports to confirm that good laboratory practices were being followed with regard to lab methods, detection limits, spiked samples, etc.

Both laboratories evaluated accuracy by preparing and analyzing duplicate spiked samples. The matrix spiked and matrix spiked duplicate (MS/MSD) results were included in the QA/QC review. The parameters which had MS/MSD evaluations were sulfate, chloride, nitrate-nitrite, total phosphorous, total metals, dissolved metals, total organic carbon, and dissolved organic carbon.

4.2.a Data Submission

The data reports from the laboratory were sent to the EPA QA/QC staff. The following additional items were included in each laboratory report: Name and location of laboratory; signature of the Laboratory Director (approval signature); project name; report date; stations; date and time of sampling; laboratory sample ID; listing of all problematic quality control items (for that set of samples) and supporting documentation of the necessary corrective action/s; analytical methods used for each parameter; date of analysis for each analyte; units; analytical results; results for laboratory and field blanks (field blanks are identified by samplers to the lab); sequential page number with total number of pages indicated; fully defined header information with tables of QC results; QC acceptance limits for each QC result; results of preservations checks; MDLs for each analyte and referenced procedure; the QC results summary in each data package is to be limited to that associated with the samples in a months data package; the date and time or position in the analysis sequence of the analysis of QC sample (included in each QC sample result summary for each month); quantitation limits and a reference to method for establishing the QL (e.g. $\geq 3 \times \text{MDL}$); and all calibration, analysis run logs, and sample “raw data” (instrument readings) for the key sites and parameters monitored, to allow the reconstruction of the analytical results, as part of data validation for this project. Additional supporting analytical data was requested if problems were encountered in performing the data validation. The report included the analytical results for the sample set, any QA/QC problems encountered during the analyses; changes in the QAPP; and data quality assessment in terms of precision, accuracy, representativeness, completeness, and comparability.

EPA chemists developed checklists and codes for different QA/QC issues or concerns they might find. They used these checklists in their review of the laboratory reports for compliance with QA/QC requirements. They made notes on the laboratory reports using the codes and guidelines they had developed. Those are described in this report in the section *Data Qualifiers or Flags*. Once the QA/QC review of the reports was completed, the original laboratory records were placed in storage. Copies of the lab reports with the handwritten codes were sent to the Project Officer and report writers.

The laboratories provided an electronic record of the chemistry results for most of the samples. The transfer of these data into the electronic database for this study is described in this report in

the section *Database of Results*.

4.2.b Data Qualifiers or Flags

EPA Region III Chemists performed the quality review of the analytical data evaluating methods, holding times, preservatives, minimum detection limits (MDL), back calculation of results from lab bench sheets, and compliance with good laboratory practices. Based on this review they assigned “Qualifiers” or “flags” to the data. In general the qualifiers were either Estimates or Rejects.

Estimate codes were assigned in the following categories:

- B No filter blank for DOC or Dissolved Metals, or the blank results exceed 1/10 the sample results.
- C Calibration not performed or documented, or the results vary from the standard concentration by more than 20%.
- D Minimum Detection Limit exceeds QAPP specifications.
- H Holding Times not documented or beyond specification in 40 CFR Part 136.
- M Method not specified or not complying with 40 CFR Part 136.
- P Proper preservative not used or not documented.
- Q Matrix spikes outside of specifications for recovery limits (either lab limits or +/- 25%) or RPD of duplicate spikes beyond precision limits (either lab limits or < 20% RPD). 10 % of samples for selected parameters were to include a matrix spike.
- ? Other (e.g. N.D. = no raw data to support result for critical stations and parameters).

Reject codes were assigned for the following categories:

- R(H) Holding time two days or more beyond the required holding time.
- R(B) Sample value did not exceed the level in the laboratory blank or field blank.
- R(?) Reject for other specified reason.

These flagging codes were hand written on the lab reports during the QA/QC review by the Chemists. EPA staff reviewed the coded lab reports and identified all the data flagged as Rejected. Some additional data was rejected after further evaluation by the report writers after reviewing field and lab notes. These “flags” were entered in the electronic spreadsheet for this study and cross checked for data entry errors. **No rejected data has been included in any statistical evaluations of stream quality for this study.**

Significant amounts of data from the first lab were rejected in the QA/QC review. Roughly 60 % of the values were rejected for Total Suspended Solids, Total Dissolved Solids, Total Phosphorous, and Total Mercury. Overall about 20% of the entire data set from the first laboratory rejected. The data quality from the second laboratory was much better. The second laboratory had fewer problems with excessive holding times and very little contamination of blanks. The same codes for data qualifiers or flags were used by the EPA Chemists reviewing the data. Again codes were manually written on a lab report form and EPA staff reviewed the coded lab reports and identified all the data flagged as Rejected. They entered these “flags” in the electronic spreadsheet for this study and cross checked this entire data entry effort. **No rejected data has been included in any statistical evaluations of stream water quality for**

this study.

4.2.c Laboratory Data Completeness Evaluation

Completeness of the entire data set varies with each parameter and with each laboratory. Completeness is calculated according to the following equation:

$$C = ((N - R) \div N) \times (100)$$

where: C = percent completeness

N = total number of values

R = number of values flagged as Rejected

The percent completeness of each parameter is included in Table 5. The percent completeness for the entire dataset is 89.7 %, just missing the goal of 90%. The first laboratory achieved 82.77 % while the second laboratory achieved 97.88 %. The most common cause of rejection was when the first laboratory failed to perform the analyses within the holding times specified in the Method. This was especially true for sulfate, chloride, total suspended solids, total dissolved solids, mercury, nitrate, and nitrite. Even though the second laboratory achieved 100 % completeness for sulfate, chloride, total suspended solids, total dissolved solids, and total phosphorous, the overall percent completeness for those parameters fell short of the goal of 90%. The second laboratory analyzed for (NO₂+NO₃)-N instead of nitrate and nitrite so the percent completeness values for those each of those parameters is from only one laboratory. The data in Table 5 indicate that several other parameters were analyzed at only one laboratory. Several parameters were reported at the second laboratory only due to automated procedures which include groups of parameters, beyond what was tested at the first laboratory.

The changes to levels of organic nutrients in the stream was a concern which initiated the monitoring for total organic carbon (TOC) and dissolved organic carbon (DOC). The values found in this study were consistently near the limits of measurability and there appeared to be something leach from the filter which interfered in the analysis causing the dissolved concentration to be higher than the total concentration. For this reason many of the values for TOC and DOC were rejected, resulting in the very low percent completeness for those two parameters. Several values for total and dissolved metals were also rejected in the QA review when the dissolved value exceeded the total value. This resulted in the lower percent completeness values for aluminum, iron and manganese.

TABLE 5
Percent Completeness for Analytical Results by Laboratory

ANALYTE	UNITS	LAB 1 - # SAMPLES	LAB 1 - # SAMPLES NOT REJECTED	LAB 1 - % COMPLETE	LAB 2 - # SAMPLES	LAB 2 - # SAMPLES NOT REJECTED	LAB 2 - % COMPLETE
ACIDITY	mg/l	266	208	78.20	191	191	100.00
ALKALINITY	mg/l	266	265	99.62	213	213	100.00
ALUMINUM, DISSOLVED	ug/l	266	234	87.97	213	213	100.00
ALUMINUM, TOTAL	ug/l	266	221	83.08	213	212	99.53
ANTIMONY, TOTAL	ug/l	266	251	94.36	213	213	100.00
ARSENIC, TOTAL	ug/l	266	264	99.25	213	213	100.00
BARIUM, TOTAL	ug/l				213	213	100.00
BERYLLIUM, TOTAL	ug/l	266	257	96.62	213	213	100.00
CADMIUM, TOTAL	ug/l	266	266	100.00	213	213	100.00
CALCIUM, TOTAL	ug/l	266	264	99.25	213	213	100.00
CHLORIDE	mg/l	266	161	60.53	213	213	100.00
CHROMIUM, TOTAL	ug/l	266	245	92.11	213	213	100.00
COBALT TOTAL	ug/l				213	213	100.00
COPPER, TOTAL	ug/l	266	255	95.86	213	211	99.06
DISSOLVED, ORGANIC CARBON	mg/l	266	208	78.20	213	170	79.81
HARDNESS, TOTAL	mg/l				212	212	100.00
IRON, DISSOLVED	ug/l	266	222	83.46	213	208	97.65
IRON, TOTAL	ug/l	266	208	78.20	213	205	96.24
LEAD, TOTAL	ug/l	266	255	95.86	213	213	100.00
MAGNESIUM, TOTAL	ug/l	266	266	100.00	213	213	100.00
MANGANESE, DISSOLVED	ug/l	266	228	85.71	213	210	98.59
MANGANESE, TOTAL	ug/l	266	218	81.95	213	210	98.59
MERCURY, TOTAL	mg/l	266	129	48.50	213	174	81.69
NICKEL, TOTAL	ug/l	266	239	89.85	213	213	100.00
NITRATE+NITRITE (N)	mg/l				212	199	93.87
NITRATE	mg/l	266	144	54.14			
NITRITE	mg/l	266	175	65.79			
PHOSPHORUS, TOTAL	mg/l	266	106	39.85	213	213	100.00
POTASSIUM, TOTAL	mg/l	266	264	99.25	213	213	100.00
SELENIUM, TOTAL	ug/l	266	259	97.37	213	210	98.59
SILVER, TOTAL	ug/l	266	266	100.00	213	213	100.00
SODIUM, TOTAL	mg/l	266	265	99.62	213	213	100.00
SULFATE	mg/l	266	171	64.29	213	213	100.00
THALLIUM, TOTAL	ug/l	266	250	93.98	213	213	100.00
TOTAL DISSOLVED SOLIDS	mg/l	266	116	43.61	213	213	100.00
TOTAL ORGANIC CARBON	mg/l	266	206	77.44	213	180	84.51
TOTAL SUSPENDED SOLIDS	mg/l	266	115	43.23	213	213	100.00
VANADIUM, TOTAL	ug/l				213	213	100.00
ZINC, TOTAL	ug/l	266	244	91.73	213	199	93.43
TOTALS FOR EACH LAB		9310	7706	82.77	7857	7690	97.88044
OVERALL % COMPLETENESS							89.70

4.3 Corrective Actions

There was a problem early in the study with the field crews not collecting the proper number of Field Duplicate samples. None were collected during the first four rounds of samples. The problem was resolved through increased communication and coordination with the laboratory and field crews. From March through the end of the study, the crews usually collected one duplicate sample every day they were sampling. Field Duplicates made up more than 10% of the samples being collected after March of 2000.

There was also a problem early in the study with the field crews not collecting Blank Samples each day which were to be processed and analyzed just like the stream samples. There was continuing confusion regarding collection and preservation of Blank Samples. Some field crews collected two sets of Blank Samples each day calling one set a Trip Blank and the other set a Field Blank. There was also an intermittent problem with some crews not having adequate supplies of sample containers and lab pure water for the blanks. There was a meeting to improve coordination with the field crews and the laboratory prior to the start of work with the second laboratory, but the Blanks continued to be called different names by different crews.

There were problems with the quality of laboratory data and supporting information during this study forcing a change of laboratories performing the analyses. Timely submission of the laboratory data for QA review by EPA staff was a problem throughout the study. Corrective actions taken included requiring submission of corrections to laboratory reports and submission of additional records. The improvement in percentage completeness between the two laboratories indicates success of the corrective actions.

4.4 Database of the Results

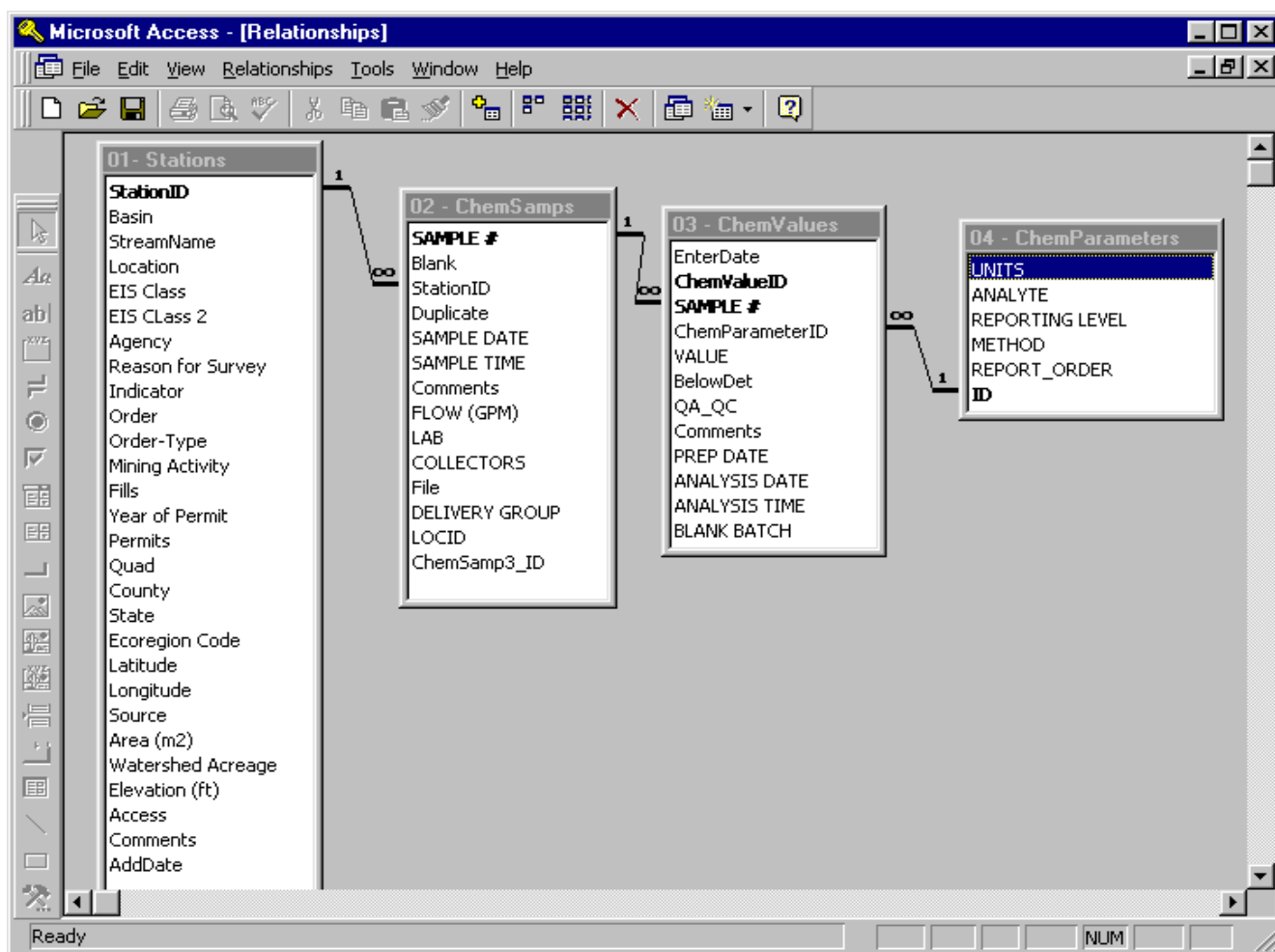
The evaluation of the large amount of data collected during this study has been facilitated by compiling it in an electronic database. Much of the results of analyses from both laboratories were provided to EPA in an electronic format. These data were merged into a single database. This process included standardizing field names, chemical parameter names, and units of measurement. The mountaintop mining chemistry database was established using the Microsoft Access97® relational database. It is included in this report as APPENDIX 3. The database is compatible with most other database software. It can be linked to other applications such as ArcView®, ArcInfo®, or USEPA's STORET. Figure 2 illustrates how the database is organized. The chemistry database contains a collection of four tables that are linked by one or more fields in order to facilitate data analysis. Information regarding each sampling site is listed in the table *01-Stations*. Information about each sample is in the table *02-ChemSamps*. Laboratory results for each sample are stored in the table *03-ChemValues*. Information about the chemical parameters is in the table *04-ChemParameters*. This vast amount of information was separated into four tables to reduce repetition within the database.

At least one field in each of the tables is the primary key for the table which functions as a

unique identifier for the information stored in that table. Primary keys are used to link the tables to one another using one-to-many relationships. For example, the field *StationID* is the primary key for table *01 - Stations* and is used to link to table *02 - ChemSamps*. *StationID* is not duplicated in table *01 - Stations*, but it is duplicated in table *02-ChemSamps* because stations were sampled multiple times in this study.

Figure 2.
Organization of Database

Not all the chemical analyses were provided in electronic form from the laboratories. Four



months of lab chemistry data and field chemical parameters for all of the samples were only available in paper form. This data was entered into the database by EPA staff using a set of data entry forms they created to simplify and standardize the data entry process. Staff at the Wheeling office completed an independent check of 100% of the data entry performed at Wheeling and also checked the remainder of the values in the database against the paper copies of laboratory reports and field sheets. Additional checks on the quality of the data and data entry were made

using queries of the database. A request to retrieve or manipulate data from the database is called a query. Queries can filter and summarize data from one or more of the database tables by setting specific criteria and then displaying the results in tabular form. For example, queries can select specific data such as finding all of the samples where a particular value is greater than a specified water quality criteria. They can also perform functions such as calculating hardness from total calcium and total magnesium values. Range checks were performed using queries for each parameter. They provided an extra indication of the accuracy of the data entry since outliers were again verified using the original lab reports. The range checks were useful because they indicated a group of samples where the values for dissolved aluminum, iron and manganese were reported by the laboratory using incorrect units. This problem was then resolved with a letter from the laboratory correcting the errors. An examination of the range of the data also highlighted the importance of considering the values reported for blank samples and highlighted temporal and/or laboratory differences for several chemical parameters.

As a result of QA/QC verification and validation procedures, additional information was added to the original database preserving the original data, but allowing for a record of QA/QC evaluations. The *03-ChemValues* table contains a *QA_QC* field for recording data “flags”. A “R” was placed in the QA field for chemistry values that were rejected in the QA/QC data review. Likewise a “B” was added to the QA field when the laboratory results for blanks was greater than or equal to 10% of the sample results. A “RWHL” was entered in the *QA_QC* field where the report writers identified problems with the data such as when the value for dissolved organic carbon was greater than the value for total organic carbon or when a note from the chemist indicated acid appeared to have been added to the wrong sample container. Some other values were rejected based on the field sheet notes of problems encountered at the time of sampling. For example, the field sheet for one sample noted they only acidified bottles 2 & 6. These field sampling problems were flagged “RWHL” and the appropriate values were rejected from the data evaluation.

5. EVALUATION AND DISCUSSION OF RESULTS

Several methods of evaluating the data were undertaken in seeking to characterize and compare conditions in streams below mountaintop removal / valley fill mining operations. This evaluation was made more complicated by several factors including variations in the quality of the data. The precision of sampling results varied with each parameter as well as with laboratory over the duration of the study. The results of the duplicate samples and blank samples are used to assess the precision of sample results and better evaluate the true impact. This evaluation was facilitated by storing the data in an electronic database which is described first in this evaluation and discussion.

The initial evaluation seeks to identify **parameters likely to be impacted by MTM/VF mining**. The average water quality at all Filled sites is compared to the water quality at all Unmined sites sampled during this study. The parameters most altered are then examined for all categories of sites for the entire data set to evaluate mining impacts on each parameter. Variations in data quality are evaluated using the duplicate sample results. Additional insight is provided through calculation of a value called “Yield,” an idea taken from a USGS publication (Sams & Beer 2000, page 10). Yield rates are calculated by dividing loading values by the drainage area.

The second approach in this evaluation is to identify the samples and sites which **exceeded West Virginia’s stream water quality criteria**. Sites which have multiple violations are described and characterized.

Finally, the eight parameters which had **little or no detectable concentrations** in any samples are listed and briefly discussed.

5.1 Parameters Likely To Be Impacted By MTM/VF Mining

5.1.a Filled Sites vs Unmined Sites

The median concentration from all Filled sites was compared to the median concentration from all Unmined sites to identify which parameters were most likely to be impacted by MTM/VF mining. The ratio of Mined to Unmined was used to prioritize the discussion and evaluation of the data from all categories of sites. Only data from the second laboratory was used in this comparison since there were data quality differences between the two laboratories. Table 6 lists the median values for all Filled site data and all Unmined site data as well as the ratios for each parameter. There are 16 parameters with a ratio greater than 1.0 and each will be discussed individually beginning with sulfate. The 25 remaining parameters will also be discussed but they may be discussed in groups of parameters or in later sections of this report.

Table 6. Median Values at All Filled vs All Unmined Sites - Lab 2 Only

<i>Parameter</i>	<i>Median Unmined*</i>	<i>Median Filled*</i>	<i>Ratio Filled/Unmined</i>	<i>Det. Limit @ Lab 2*</i>
Sulfate	12.55	523.5	41.7	5
Calcium	4.875	104	21.3	0.1
Magnesium	4.095	86.7	21.2	0.5
Hardness	29.05	617	21.2	3.31
Solids, Dissolved	50.5	847	16.8	5
Manganese, Total	0.005	0.04395	8.8	0.01
Conductivity, Field (uS/cm)	66.4	585	8.8	N/A
Selenium	0.0015	0.01168	7.8	0.003
Alkalinity	20	149.5	7.5	5
Potassium	1.58	8.07	5.1	0.75
Sodium	1.43	4.46	3.1	0.5
Manganese, Dissolved	0.005	0.01035	2.1	0.01
Chloride	2.5	4.5	1.8	5
Acidity	2.5	4.25	1.7	2
Nitrate/Nitrite (N)	0.81	0.95	1.2	0.1
pH, Field (std)	6.78	7.77	1.1	N/A
Acidity, Hot	2.5	2.5	1.0	5
Aluminum, Dissolved	0.050	0.050	1.0	0.1
Antimony	0.0025	0.0025	1.0	0.005
Arsenic	0.001	0.001	1.0	0.002
Beryllium	0.0005	0.0005	1.0	0.001
Cadmium	0.0005	0.0005	1.0	0.001
Chromium	0.0025	0.0025	1.0	0.005
Cobalt	0.0025	0.0025	1.0	0.005
Copper	0.0025	0.0025	1.0	0.005
Lead	0.001	0.001	1.0	0.002
Mercury	0.0001	0.0001	1.0	0.0002
Nickel	0.010	0.010	1.0	0.02
Organic Carbon, Total	1.35	1.4	1.0	1
Phosphorous	0.05	0.05	1.0	0.1
Silver	0.005	0.005	1.0	0.01
Thallium	0.001	0.001	1.0	0.002
Vanadium	0.005	0.005	1.0	0.01
Barium	0.02885	0.02465	0.9	0.02
Dissolved Oxygen, Field	13.6	11.045	0.8	N/A
Organic Carbon, Dissolved	2.45	1.95	0.8	1
Solids, Suspended	5.75	4.25	0.7	5
Iron, Total	0.417	0.1935	0.5	0.1
Iron, Dissolved	0.220	0.096	0.4	0.1
Zinc	0.006	0.0025	0.4	0.005
Aluminum, Total	0.147	0.050	0.3	0.1

* Concentrations are in mg/L unless noted.

5.2 Sulfate Data

Although there is no stream criterion for sulfate in West Virginia to protect aquatic life, several groups have looked at the impacts of sulfate on other water uses. The adverse effects of high concentrations of aluminum in water supplies were noted in EPA's "Blue Book 1972." Their recommendation was:

On the basis of taste and laxative effects and because the defined treatment process does not remove sulfates, it is recommended that sulfate in public water sources not exceed 250 mg/l where sources with lower sulfate concentrations are or can be made available. (Rolich et al 1972, page 89)

This recommendation was set to protect human health at water supplies using surface waters as a source. Additional research should be conducted to investigate the effects of sulfates on aquatic life. Regarding the impact on aquatic life, the California State Water Resources Control Board publication *Water Quality Criteria* 1963 edition states:

In U.S. waters that support good game fish, 5 percent of the waters contain less than 11 mg/l of sulfates, 50 percent less than 32 mg/l, and 95 percent less than 90 mg/l. Experience indicates that water containing less than 0.5 mg/l sulfate will not support growth of algae. (McKee et al 1963, page 276)

MTM/VF permit writers in West Virginia recognize sulfates as a significant indicator of mining activity. Their Cumulative Hydrologic Impact Assessment (CHIA) report for the Twentymile Creek watershed states:

The data indicate that the sulfate concentrations are increased with mining. Sulfates are endemic to mining areas and are indicators of mining in a watershed. A rule of thumb can be observed from the water quality data researched for this CHIA. This rule is (A) below 20 mg/l there is no mining in the watershed (B) between 20 and 30 mg/l there has been very little or no impact from mining in a watershed (C) from 30 to 100 mg/l there has been some impact from mining (D) above 100 mg/l there has been certain impact from mining. (West Virginia Department of Environmental Protection, CHIA for Twentymile Creek, pages not numbered)

5.2.a Sulfate Concentration in Stream Samples

The concentration of sulfate at each site varied with time during this study. The values for each sample from all sites have been plotted against time in Figure SO₄-1. Each category of site has been plotted with a different symbol so the variation of concentrations classes of sites can be evaluated. The detection limit was 10 mg/L at the first laboratory and 5 mg/L at the second laboratory.

The sulfate concentrations at the Unmined sites fit the rule of thumb for unmined watersheds set by the CHIA report writers and were well below the recommended drinking water criterion of 250 mg/l. The median concentration for all Unmined sites was only 14.25 mg/L. The US Geological Survey report Water Quality in the Allegheny and Monongahela River Basins, Circular 1202", published in 2000 indicates the regional background concentration of sulfate in unmined watersheds in the northern portion of the Appalachian coal field averages about 21 mg/l (Anderson et al 2000, page 20), which is similar to the concentrations at Unmined sites in this study.

Many samples from the categories Filled and Mined had sulfate values exceeding the recommended drinking water standard of 250 mg/L. Especially noteworthy are the values for the samples from site MT-24, a yellow diamond symbol in Figure SO₄-1. The concentrations ranged from 800 to 2,300 mg/L and are consistently higher than the concentration at all other types of sites. This site is not a stream but a flow diversion ditch at an MTM/VF mine. Obviously the site is a source of sulfate to the stream below. The sites in the category Filled comprise the majority of the higher concentrations.

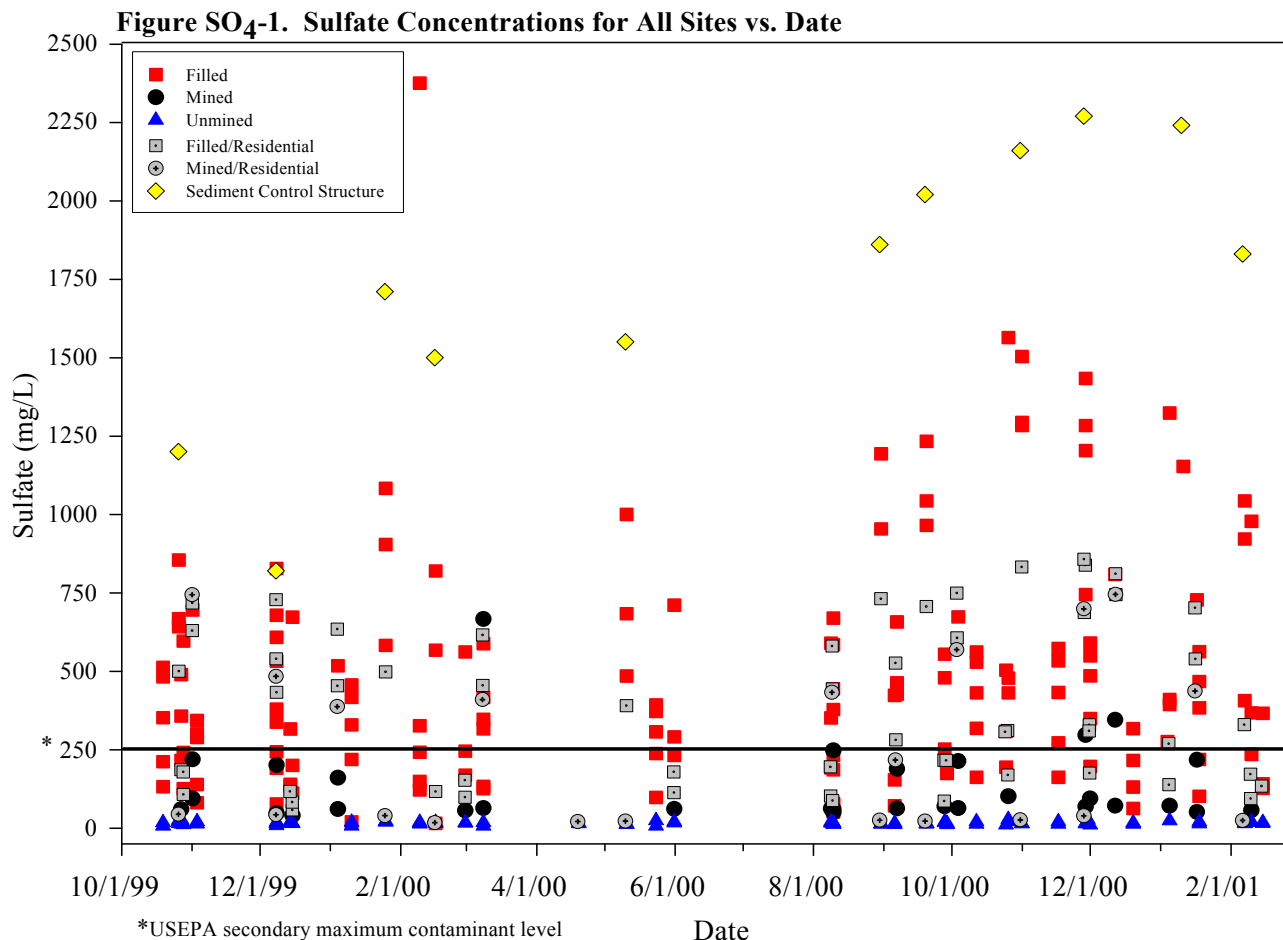


Table SO₄-1 lists a summary of the 172 samples which exceed the Secondary Maximum Contaminant Level of 250 mg/L for Sulfate. Roughly 45 % of the samples which passed the QA/QC review exceeded the sulfate criterion but none came from sites in the category Unmined. There are 110 samples from the category Filled, and another 37 samples from the category Filled/Residences. There are 4 samples at Mined sites and another 10 from the category Mined/Residences. There were 11 samples from the diversion ditch exceeding the criterion. The sites where the sulfate concentration was high were scattered across the study area in areas where coal mining has occurred.

Table SO₄-1. Number of Samples Exceeding the Secondary Maximum Contaminant Level of 250 mg/L for Sulfate

Station ID	EIS Class	No. Samples > 250 mg/L
MT-14	Filled	10 of 11
MT-15	Filled	10 of 10
MT-18	Filled	11 of 11
MT-25B	Filled	7 of 10
MT-32	Filled	4 of 10
MT/34B	Filled	10 of 10
MT-52	Filled	3 of 8
MT-57B	Filled	6 of 7
MT-64	Filled	11 of 11
MT-87	Filled	3 of 13
MT-98	Filled	13 of 13
MT-103	Filled	12 of 13
MT-104	Filled	10 of 13
MT-23	Filled/Residences	10 of 11
MT-48	Filled/residences	3 of 10
MT-55	Filled/Residences	2 of 8
MT-62	Filled/Residences	11 of 11
MT-75	Filled/Residences	11 of 11
MT-79	Mined	4 of 11
MT-69	Mined/Residences	10 of 11
MT-24	MTM/VF Diversion Ditch	11 of 11

5.2.b QA Samples for Sulfate

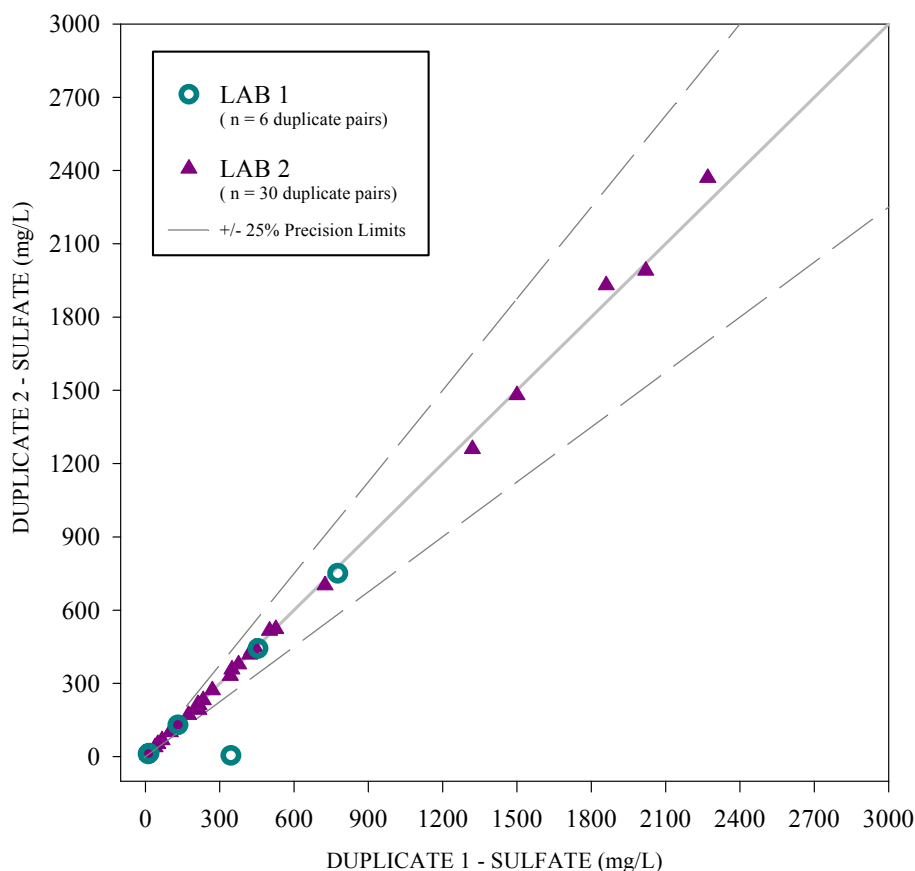
Evaluation of the results of duplicate samples indicate the values for sulfate are generally precise. The QA/QC review of the data checked for accuracy. The sulfate data remaining are suitable for evaluating the impacts to stream chemistry resulting from MTM/VF mining. The Relative Percent Difference (RPD) values for the 44 sets of field duplicate samples are listed in Table SO₄-2.

Table SO₄-2. RPD for Field Duplicates for Sulfate

Station ID	Sample Date	Laboratory	RPD
MT104	3/8/00	LAB 1	194
MT62	3/8/00	LAB 1	3
MT86	3/8/00	LAB 1	1
MT02	4/19/00	LAB 1	1
MT02	5/10/00	LAB 1	1
MT75	6/13/00	LAB 1	3
MT25B	8/8/00	LAB 2	2
MT104	8/9/00	LAB 2	1
MT52	8/9/00	LAB 2	5
MT62	8/9/00	LAB 2	1
MT24	8/30/00	LAB 2	4
MT98	9/5/00	LAB 2	1
MT75	9/6/00	LAB 2	1
MT24	9/19/00	LAB 2	1
MT48	9/27/00	LAB 2	11
MT51	9/28/00	LAB 2	0
MT79	10/3/00	LAB 2	1
MT95	10/11/00	LAB 2	1
MT57B	10/24/00	LAB 2	3
MT25B	10/25/00	LAB 2	1
MT15	10/31/00	LAB 2	1
MT87	11/16/00	LAB 2	1
MT24	11/28/00	LAB 2	4
MT81	11/28/00	LAB 2	1
MT40	11/30/00	LAB 2	2
MT50	11/30/00	LAB 2	2
MT79	12/11/00	LAB 2	4
MT91	12/19/00	LAB 2	0
MT55	1/3/01	LAB 2	2
MT34B	1/4/01	LAB 2	5
MT01	1/10/01	LAB 2	1
MT64	1/16/01	LAB 2	3
MT86	1/17/01	LAB 2	0
MT02	2/6/01	LAB 2	1
MT32	2/9/01	LAB 2	1
MT55	2/14/01	LAB 2	2

The highest RPD for the duplicates was 11 and many values were 1. This indicates the data for sulfate was generally precise throughout the study. The results of duplicate samples are also presented in Figure SO₄-2, Comparison of Duplicate Samples - Sulfate Concentration. In this graph, duplicate sets of sample results are plotted with one value being plotted on the x-axis and the other plotted on the y-axis. If a set of duplicate samples had exactly the same concentration value, the point would fall on a line from zero/zero to 3000/3000. A general limit on precision of plus or minus 25% was used in this study. This precision limit is also shown on the Figure to illustrate if a set of duplicate samples are out of normal precision limits or “out of control.” In addition, the values from the two laboratories are plotted with different symbols to determine if there is a difference in precision between the data from the two parts of the study. There were nine sets of duplicate samples rejected in the QA/QC review of laboratory results, and all were during the early part of the study at laboratory 1. No duplicates were rejected in data from the second laboratory.

Figure SO₄-2. Comparison of Duplicate Samples - Sulfate Concentrations



The agreement in results for each set of duplicates is evident. Duplicate samples run at the second laboratory had a wider range of concentrations but were still quite precise.

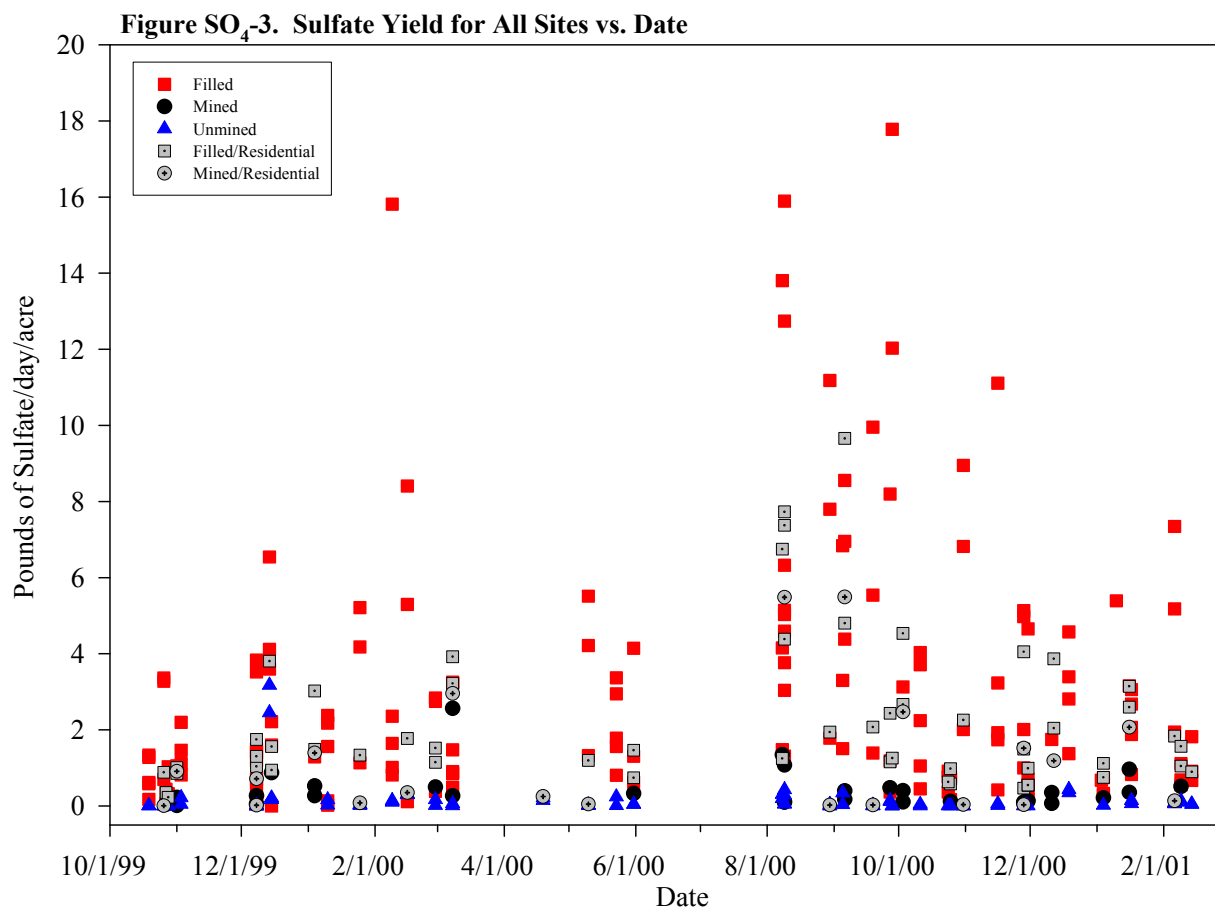
The concentration of sulfates in the 80 blank samples should have been below the detection limit. There was only one sample with a detectable concentration of sulfate and it was at the first laboratory. Of the 80 blank samples, there were 28 pairs of duplicate blank samples and all were below the detection limit in the laboratory indicating no detectable contamination occurred from sample handling in the field or the laboratory. The quality of the data for sulfate is good.

5.2.c Sulfate Yield

Sulfate has long been considered a good indicator of the presence of coal mine drainage in streams in Appalachia. The relationship between coal mining and sulfate in streams is the focus of the US Geological Survey Water-Resources Investigations Report 99-4208 (Sams & Beer, 2000). The report notes that sulfate is an excellent indicator of mine drainage because the sulfate ion is very soluble and chemically stable at the pH levels normally encountered in streams, and the treatment of mine drainage to remove metals and neutralize acidity has little or no effect on sulfate concentration. The authors calculated the annual discharge of sulfate at selected stream monitoring points and divided that loading by the drainage area above the monitoring point to determine “Sulfate Yield” in tons per year per square mile. They used these Sulfate Yield rates to rank stream degradation attributable to mining. A similar approach has been used in this report to evaluate the impacts of mining on the streams.

Sulfate Yield was calculated for each sampling event at each site. The first step was to calculate the instantaneous sulfate load for each sample event by multiplying the sulfate concentration (mg/L) times the instantaneous flow rate (cubic feet per second) times the conversion factor (5.39) to get a load in pounds per day. The Sulfate Yield was then determined by dividing the instantaneous sulfate load by the drainage area above that site. The Sulfate Yield in this report is measured in pounds of sulfate per day per acre. These Sulfate Yield values vary at each site with each sampling event. They also vary with the categories of sites being evaluated in this study - Unmined, Mined, Filled, Filled with Residences, and Mined with Residences. No Sulfate Yield values were calculated for site MT- 24 since there is no accurate data on the area now draining to the site. Mountaintop mining has changed the original drainage patterns and there is no accurate map of the new watershed boundary. The variations in Sulfate Yield can be plotted against time to compare categories of sites. Figure SO₄-3 is a graph of Sulfate Yield rates for all sites vs date.

The production of sulfate per acre at sites in the “Filled” category is much higher than at “Unmined” sites. The highest yields are consistently from “Filled” sites and range from 0 to over 14 pounds per acre per day. Sulfate Yield rates at Unmined sites are consistently less than one pound per acre per day. There are two samples collected in December 1999 at Unmined sites with yield rates greater than 2 pounds per day per acre. Those samples are from sites MT-50 and MT-51. The field sheet includes the note “Heavy precipitation in the last 24 hours,” which would explain the higher yield rate values for these Unmined sites.



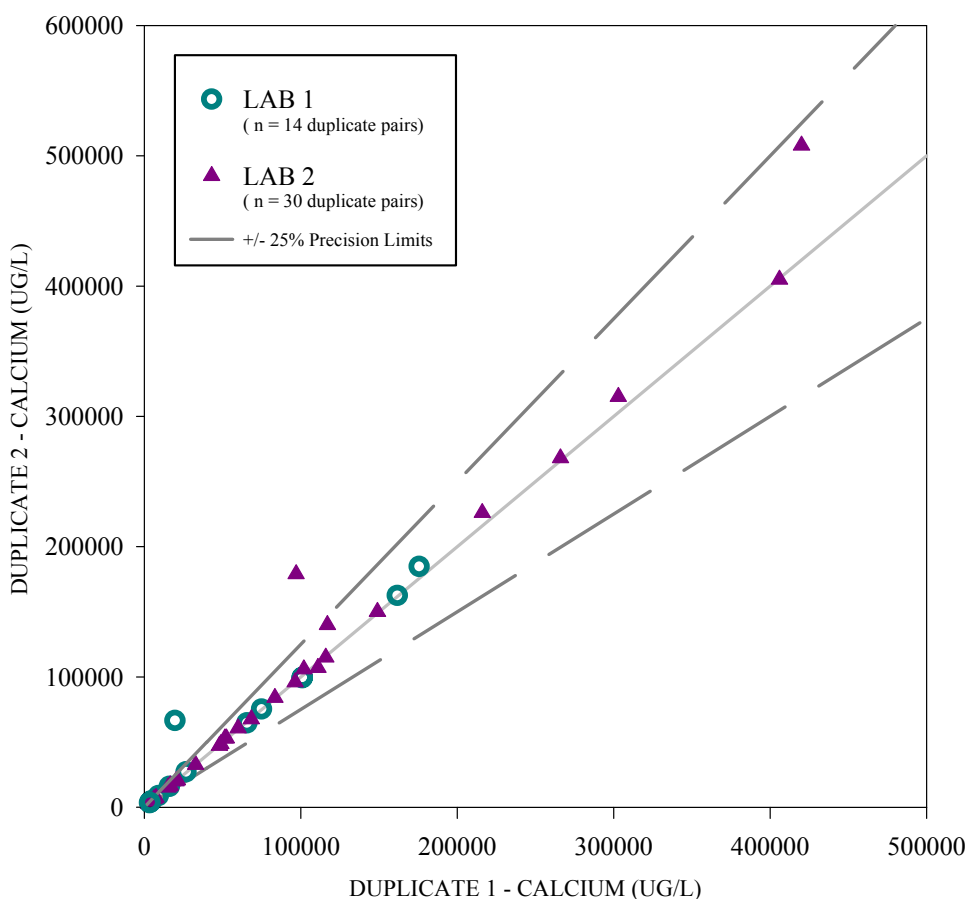
The Sulfate Yield rates described in the US Geological Survey Water-Resources Investigations Report 99-4208 (Sams & Beer, 2000) were measured in tons per year per square mile. The Yield rate for two unmined watersheds in this USGS study was calculated to be 24 tons in one watershed and 25 tons per year per square mile in another. (Sams et al 2000, page 9) This is equivalent to about 0.2 pounds per day per acre. Mined watersheds produced up to 580 tons per year per square mile (about 5 pounds per day per acre). These sulfate yield rates are for drainage areas that are many miles away from the region of mountaintop mining and have different geology. The Allegheny and Monongahela River watersheds are dominated by high sulfur coals while low sulfur coals dominate the geology of the region of mountaintop mining. Even so, the values for Sulfate Yield in the northern high sulfur region are similar to those in the study area. Unmined watersheds produce less than a pound of sulfate per day per acre and heavily mined watersheds can produce 5 pounds per day per acre or more. Sulfate is an excellent indicator of coal mining activity throughout the northern Appalachian coal field. MTM/VF mining operations increase the concentration of sulfate in streams draining the mining sites.

5.3 Calcium Data

Calcium is a significant part of hardness, but like magnesium, it does not have water quality limits. According to the California State Water Resources Control Board's *Water Quality Criteria*, calcium salts and calcium ions are among the most commonly encountered substances in water. They result from the leaching of soil and other natural sources. Calcium is an essential element for plants and animals. Concerning the impacts to fish and other aquatic life, the report notes:

Calcium in water reduces the toxicity of many chemical compounds to fish and other aquatic fauna. According to a reference cited by Hart et al., of the U.S. water supporting a good mix of fish fauna, ordinarily about 5 percent have less than 15 mg/l of calcium; 50 percent have less than 28 mg/l; and 95 percent have less than 52 mg/l.

Figure Ca-1. Comparison of Duplicate Samples - Calcium



The results of duplicate samples for calcium are shown in Figure Ca-1. The detection limit was 100 ug/L. The precision was good for both laboratories, and again there were higher values from the second laboratory. There were 13 blank samples of the 80 collected which had detectable concentrations of calcium. All were collected in the first half of this study and analyzed at the first laboratory. Further discussion of the calcium concentrations from this study will focus on the significant contribution of calcium to hardness.

5.4 Magnesium Data

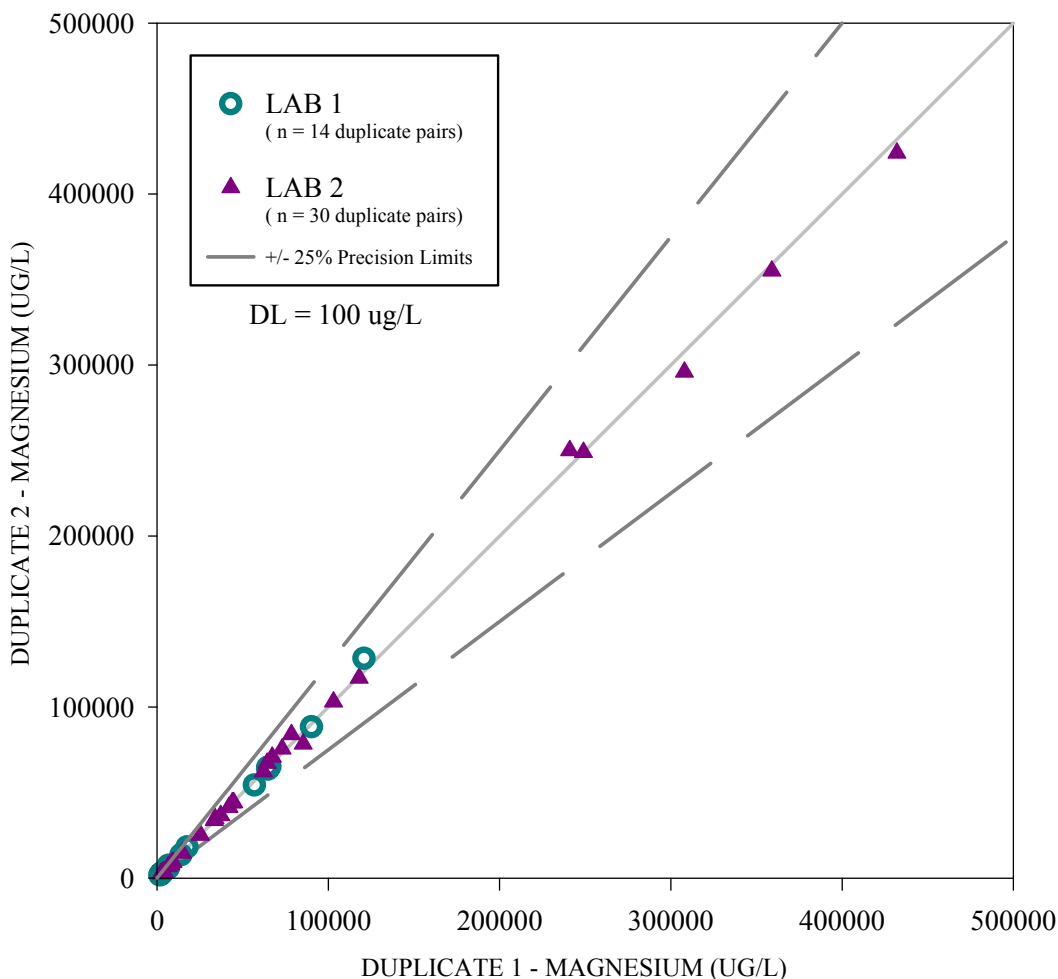
According to the California State Water Resources Control Board's *Water Quality Criteria*, magnesium constitutes about 2.1 % of the crust of the earth being widely distributed in ores and minerals. The salts of magnesium are very soluble. Magnesium is an essential element for plants and animals. Magnesium is considered relatively non-toxic to humans and not a health hazard because, before toxic concentrations are reached in water, the taste becomes quite unpleasant. Concerning the impacts to fish and other aquatic life, the report notes:

Hart et al. cite a report that among U.S. waters supporting a good fish fauna, ordinarily 5 percent have less than 3.5 mg/L of magnesium; 50 percent have less than 7 mg/L; and 95 percent have less than 14 mg/L.

The results of duplicate samples are plotted in Figure Mg-1. The detection limit was 100 ug/L. None of the laboratory values for magnesium in this study were rejected in the data quality

reviews.

Figure Mg-1. Comparison of Duplicate Samples - Magnesium



The results of duplicate samples are very precise across a wide range of concentrations. The values at the second laboratory were higher than those at the first. Ten percent of the eighty blank samples had detectable concentrations of magnesium. All of these contaminated blank samples were collected in the first half of the study. The detection limit for magnesium is 100 ug/L which is 3% of the median value detected at Unmined sites so the increase is well above the minimum detectable values. Further discussion of the magnesium concentrations from this study will focus on the significant contribution of magnesium to hardness.

5.5 Total Hardness Data

According to the California State Water Resources Control Board's *Water Quality Criteria*, the term "Hardness" refers to the soap-neutralizing power of water. Any substance that will form an insoluble curd with soap causes hardness. Hardness is attributable principally to calcium and magnesium ions but other metals can increase hardness. Indeed the standard method (Method 2340 B) for calculating hardness is determined using only the concentrations of calcium and magnesium. The equation is:

$$\text{Hardness in mg/L} = 2.497 (\text{Calcium in mg/L}) + 4.118 (\text{Magnesium in mg/L})$$

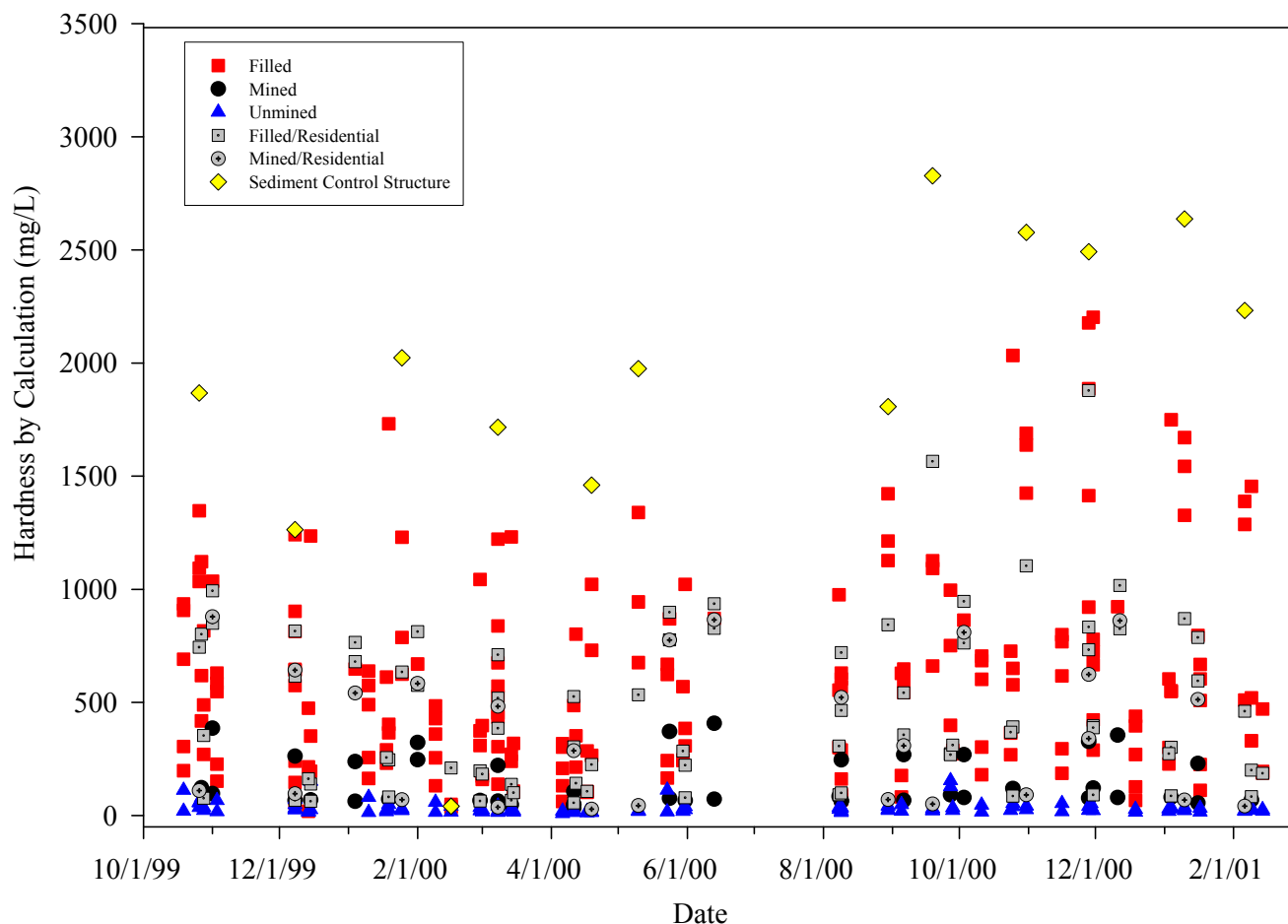
The hardness values were calculated for each sample and used in this evaluation of hardness concentration. Acceptable levels of hardness in drinking waters vary with consumer preference and "good drinking water" can have a maximum hardness from 140 mg/l to 270 mg/l. Regarding the impact of hardness on aquatic life, this reference states, "Soft water solutions increase the sensitivity of fish to toxic metals; in hard waters toxic metals may be less dangerous."

Several stream water quality criteria for toxic metals have been established with a limit that varies with the hardness in the stream. The harder the water the more of the toxic metal can be present without causing toxicity. West Virginia has set water quality limits on toxic metals to protect aquatic life in streams in this study area. These limits are calculated from equations which use the hardness concentration to calculate the maximum allowable concentration of the metal. Limits have been set for the following dissolved metals: cadmium, copper, lead, nickel, silver, and zinc. Hardness is an acceptable contaminant for most water uses in low concentrations.

5.5.a Hardness Concentration in Stream Samples

The concentration of hardness at each site varied with time during this study. The values for each sample from all sites have been calculated and plotted against time in Figure H-1. Each category of site has been plotted with a different symbol so the variations between categories can be evaluated. Unmined sites consistently have the lowest concentration of hardness while the Sediment Control Structure (MT-24) has the highest concentrations. All types of sites which have mining activity upstream also have elevated concentrations of hardness, with the Filled category sites generally being higher.

Figure H-1. Hardness Concentration for All Sites vs. Date



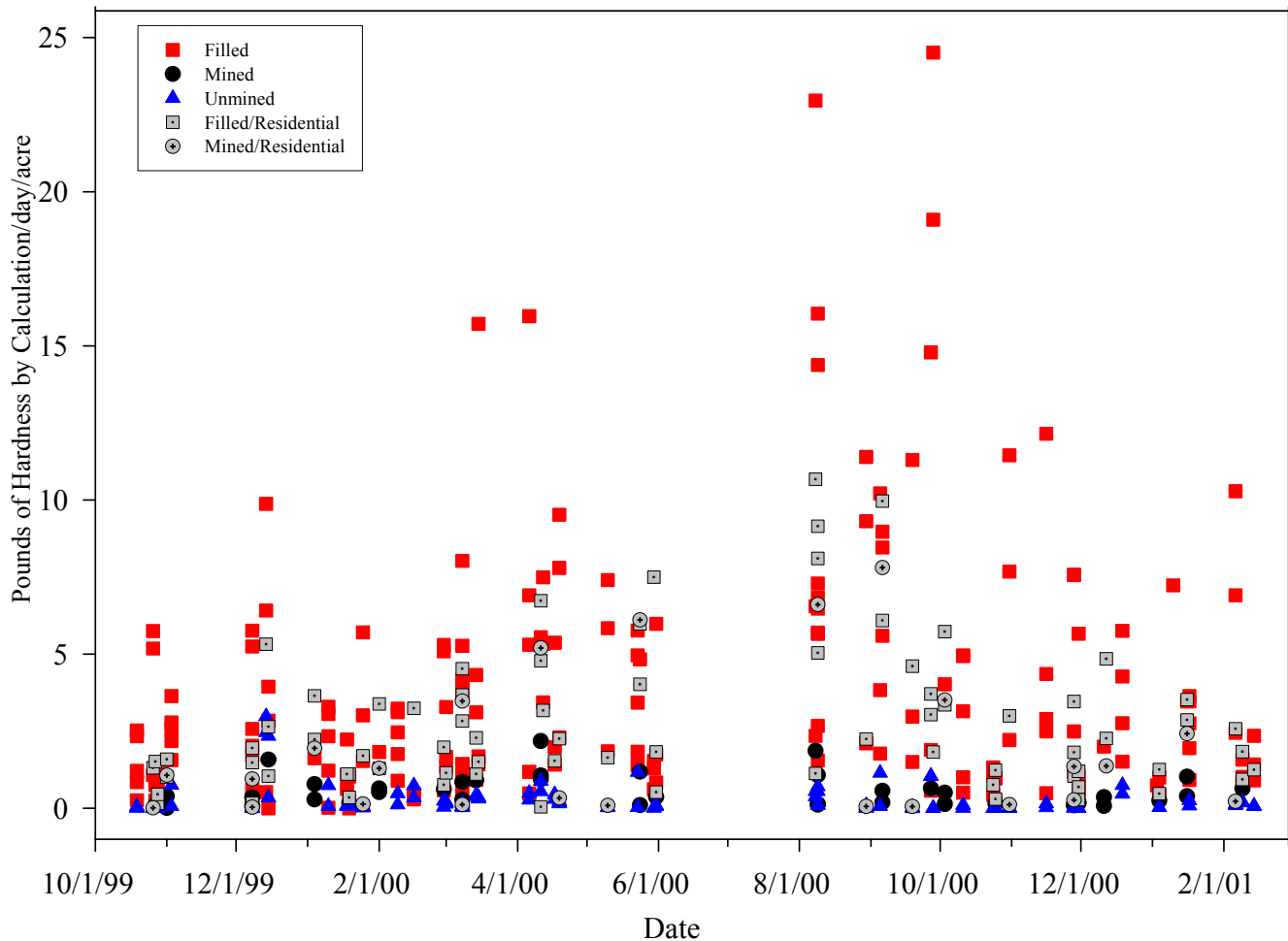
5.5.b QA Samples for Hardness

Hardness values were calculated from the concentration of calcium and magnesium. The QA samples for those parameters have been presented so there is no need for additional discussion.

5.5.c Hardness Yield

The Yield of hardness in pounds per day per acre for each sample is presented in Figure H-2. The Yield for Unmined sites is generally less than one pound per day per acre while the Yield for Filled sites is generally above two pounds per day per acre with some values nearly 25 pounds per day per acre. Higher Yields are also evident at Filled/Residential and Mined/Residential sites. There appear to be higher Yield values in the second half of the study. There are also two samples collected in December 1999 at two Unmined sites with yield rates above 2 pounds per day per acre. A note on the field sheet states “Heavy rainfall for the previous 24 hours,” which would account for these higher yield rates. The data from both laboratories indicate Filled sites have elevated values for Hardness Yield.

Figure H-2. Hardness Yield for All Sites vs. Date



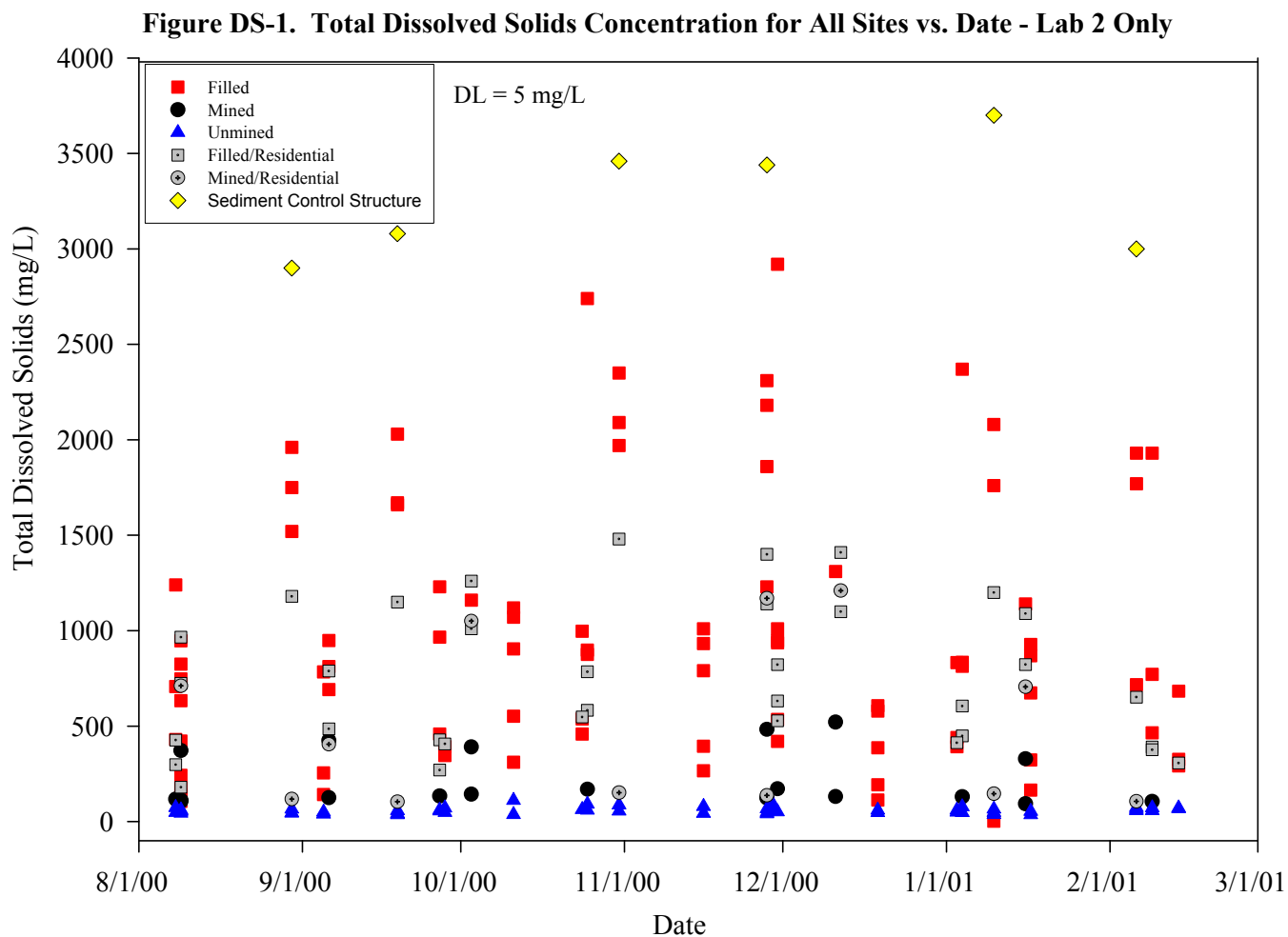
5.6 Total Dissolved Solids Data

In natural waters the dissolved solids are various minerals in their ionic form including carbonates, bicarbonates, chlorides, sulfates, phosphates, and nitrates of various metals. Since dissolved solids are often a diverse mix of various salts, the effect on use of the water can be equally diverse. For drinking water, the U.S. Public Health Service in 1962 recommended that the total dissolved solids should not exceed 500 mg/l if more suitable supplies are or can be made available. Regarding protection of fish and aquatic life, the California State Water Resources Control Board's *Water Quality Criteria* states:

It has been reported that among inland waters in the United States supporting a good mixed fish fauna, about 5 percent have a dissolved solids concentration under 72 mg/L; about 50 percent under 169 mg/L; and about 95 percent under 400 mg/L.

5.6.a Dissolved Solids Concentration in Stream Samples

Figure DS-1 presents all the data that passed the QA review for concentration of dissolved solids for all sites. The detection limit was 5 mg/L. A separate symbol represents each category of site to allow trends to be more easily observed.

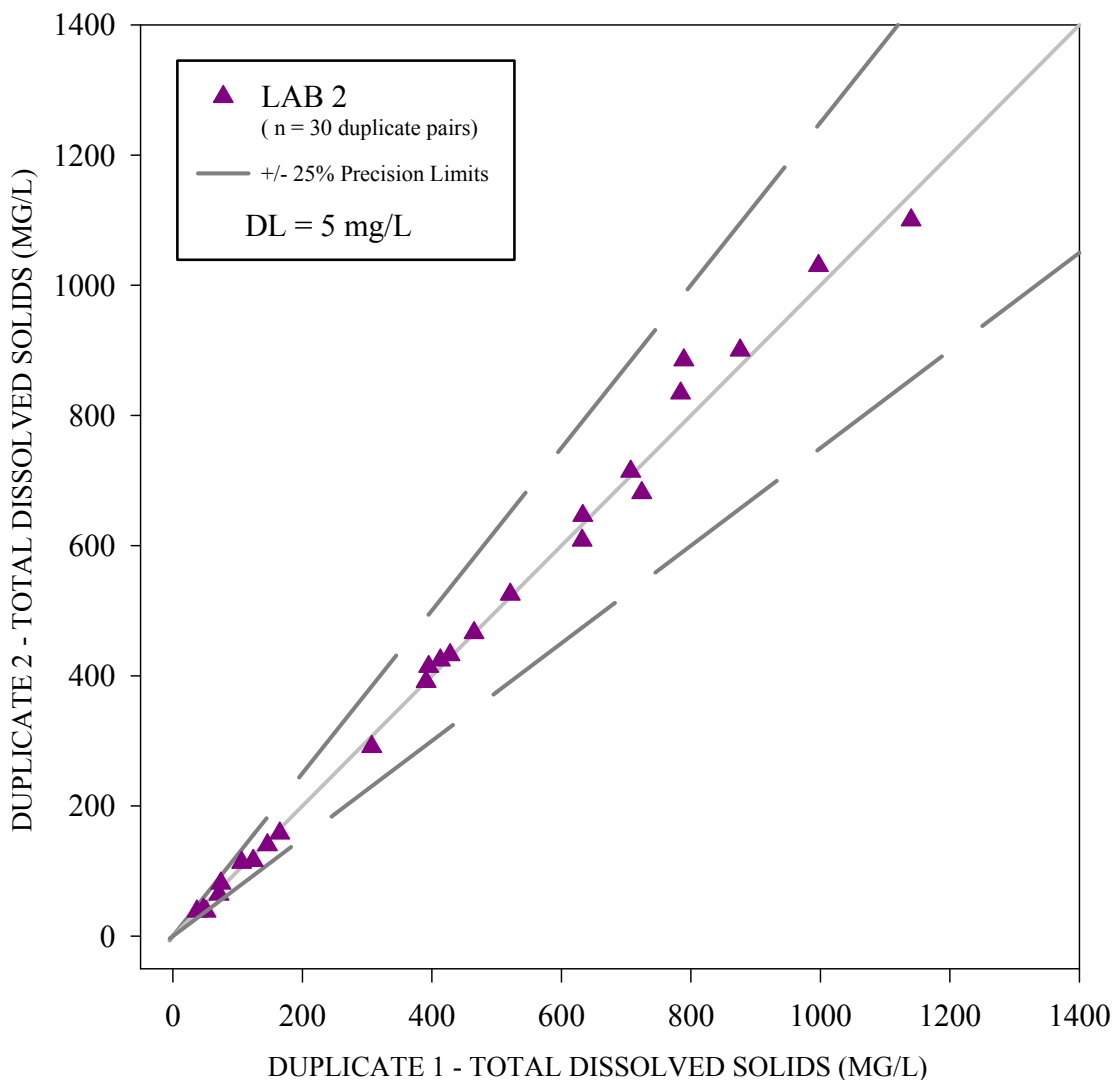


The QA review of data rejected 57 % of the values for dissolved solids at the first laboratory while 100 % of the values at the second laboratory passed the review. The values for all dissolved solids samples from the first laboratory were near zero while the values at the second laboratory range up to over 3,700 mg/L. There should have been high concentrations of dissolved solids during the first half of the study since sulfate and hardness were high. The data from the first lab was therefore not used in this evaluation.

5.6.b QA Samples for Dissolved Solids

A major reason for rejection of data at the first laboratory was excessive holding time before analysis. As for the blank samples, 27 of the 30 blanks at the first laboratory had detectable levels of dissolved solids. Only one of the 50 blanks tested at the second laboratory had measurable levels of dissolved solids. All 30 duplicate samples run at the second laboratory passed the QA/QC review. The results of duplicate samples are shown in Figure DS-2.

Figure DS-2. Comparison of Duplicate Samples-Total Dissolved Solids-Lab 2 Only



The duplicate samples results at the second laboratory are quite precise over a broad range of concentrations. The detection limit for dissolved solids was 5 mg/L which means the median value of 46 mg/L at Unmined sites is well above the limits of measurability. The dissolved solids values from the second laboratory have acceptable precision and can be used to evaluate the impacts of MTM/VF on stream water quality.

5.6.c Dissolved Solids Yield

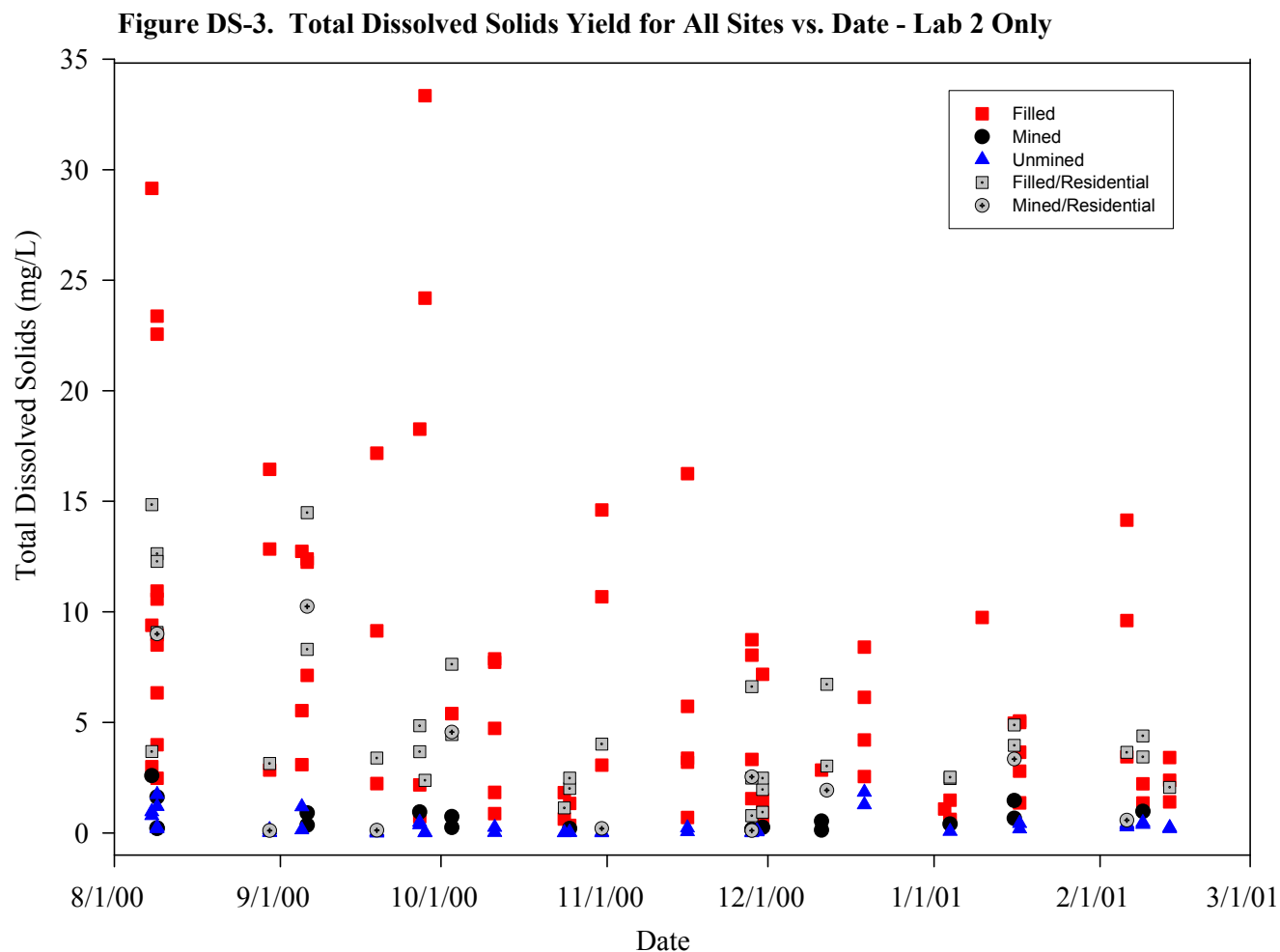


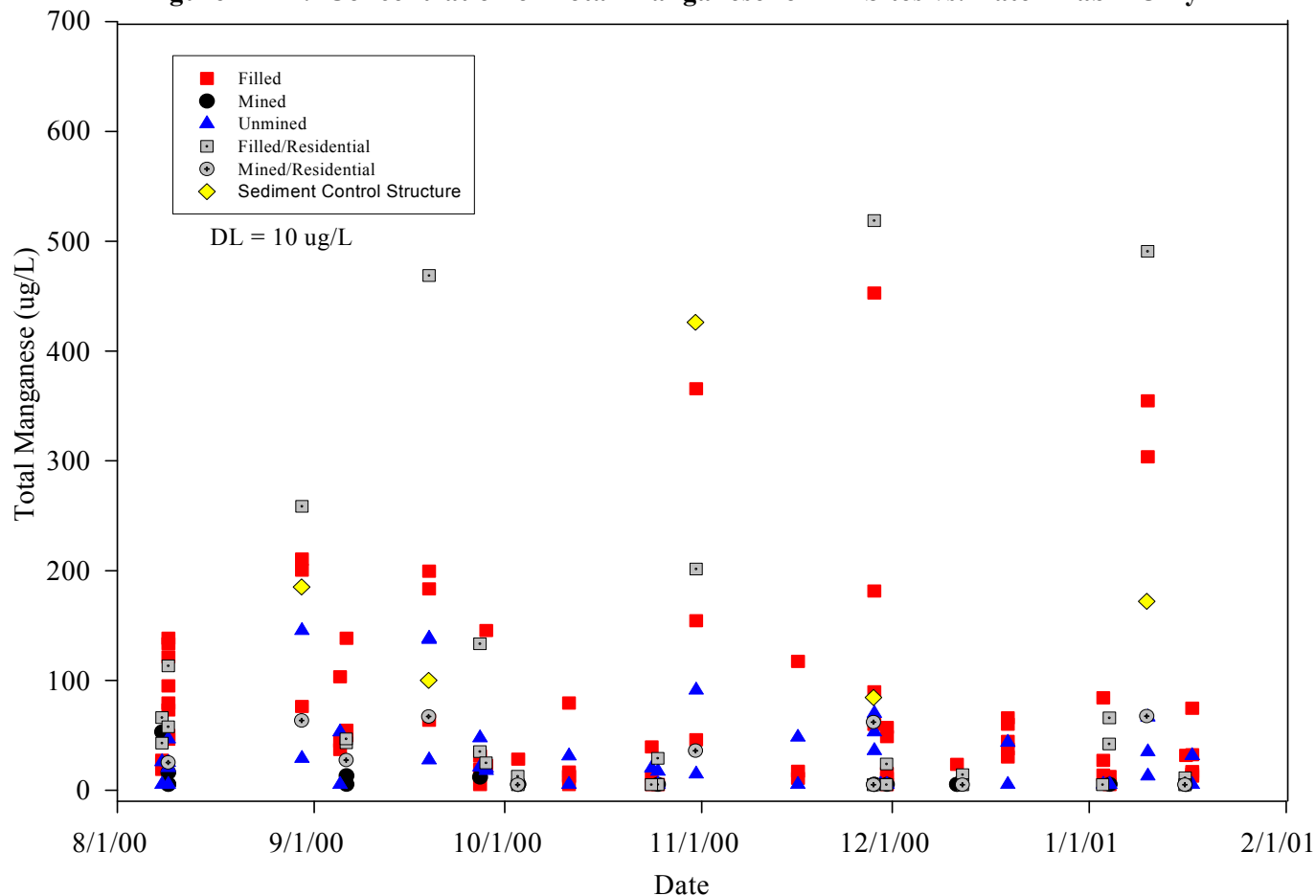
Figure DS-3 plots the Yield of dissolved solids for all sites. Yield rates for the second half of the study indicate Filled sites have elevated values of dissolved solids, up to 30 pounds per day per acre. Yield rates at Unmined sites are less than 2 pounds per day per acre.

5.7 Manganese, Total and Dissolved Data

There are discharge limits on total manganese for active mines set forth in the Code of Federal Regulations, Title 40, Part 434. The limits are 4.0 mg/L (4000 ug/L) maximum for any one day and 2.0 mg/L (2000 ug/L) maximum for thirty consecutive days. Although none of the monitoring points in this study is a discharge monitoring point for a permit, the limits serve as a reference when evaluating the concentrations in the streams. Manganese laden overburden is a concern for MTM/VF operations requiring special handling during the mining. The goal is to minimize leaching of manganese from the site in quantities that exceed the permit limit. There are reclaimed MTM/VF mines that continue to require chemical treatment of the discharges in order to comply with permit effluent limits (WVDEP CHIA for Twentymile Creek).

Data from the first lab lacked precision and was not included in this evaluation. Total manganese was detected in 70 % of the 210 samples analyzed at the second laboratory. The detection limit was 10 ug/L. It was found in all categories of sites and in all five watersheds studied. The maximum concentration of total manganese identified was 518 ug/L (site MT-23, category Filled/Residences, date - 11/28/00). This is about 12 % of the daily maximum effluent limit for coal mines. The maximum value detected at any Unmined site was 145 ug/L (MT-13, date - 08/30/00). Manganese concentration data is presented in Figure Mn-1. The higher values are generally at sites in the category “Filled”, but the values are not consistent for specific sites.

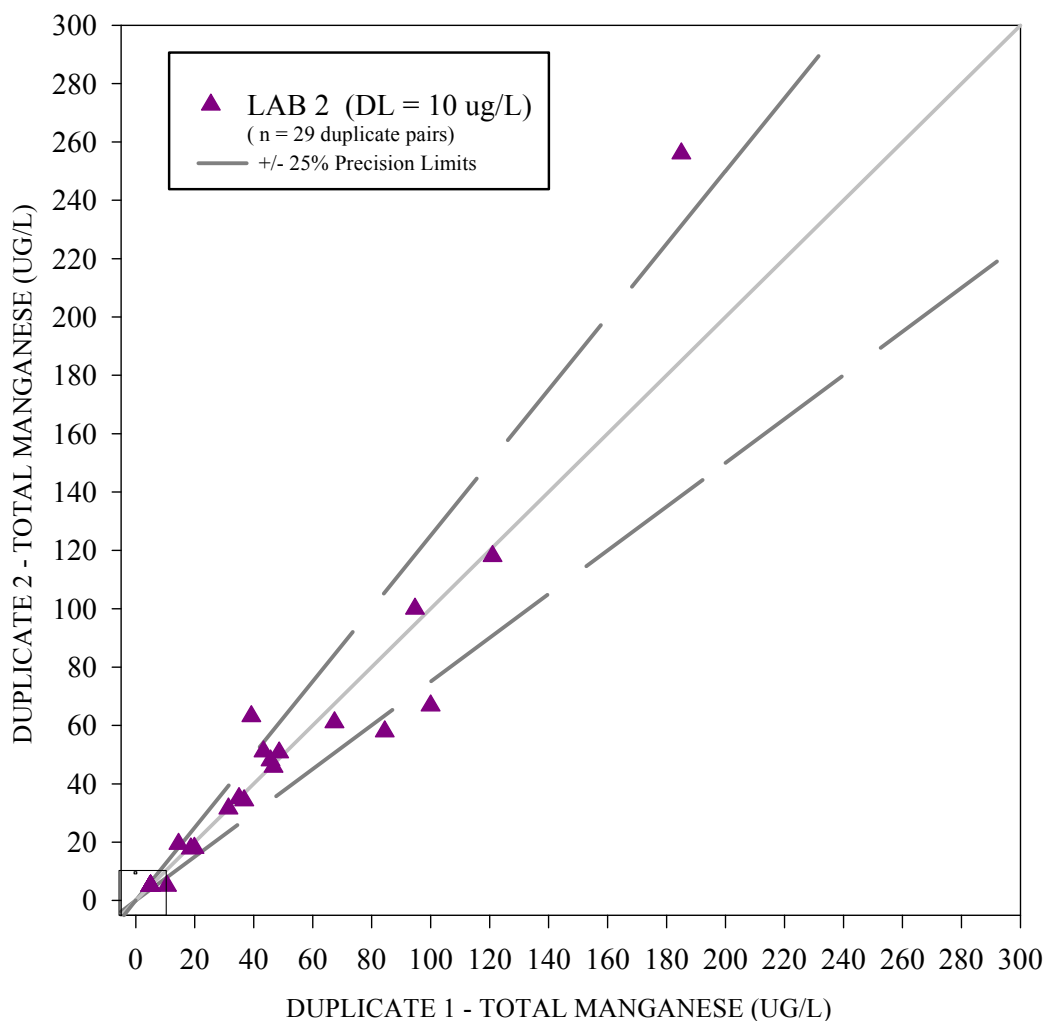
Figure Mn-1. Concentration of Total Manganese for All Sites vs. Date - Lab 2 Only



An example is range of concentrations for the Sediment Control Structure (MT-24) which go from less than 100 ug/L to more than 400 ug/L. The highest values were at site MT-23, which is the Mud River near the town of Mud. The manganese values at sites throughout the Mud River watershed are the higher values in this figure. Site MT-13, the mouth of Spring Branch in the Mud River watershed, is an Unmined site which had manganese values of 145 ug/L on 8/30/00 and 137 ug/L on 9/19/00. These higher values were associated with low flows (13 gpm and 0.5 gpm respectively) as the concentration at this site dropped below the detection limit when the flow rose to 150 gpm in February.

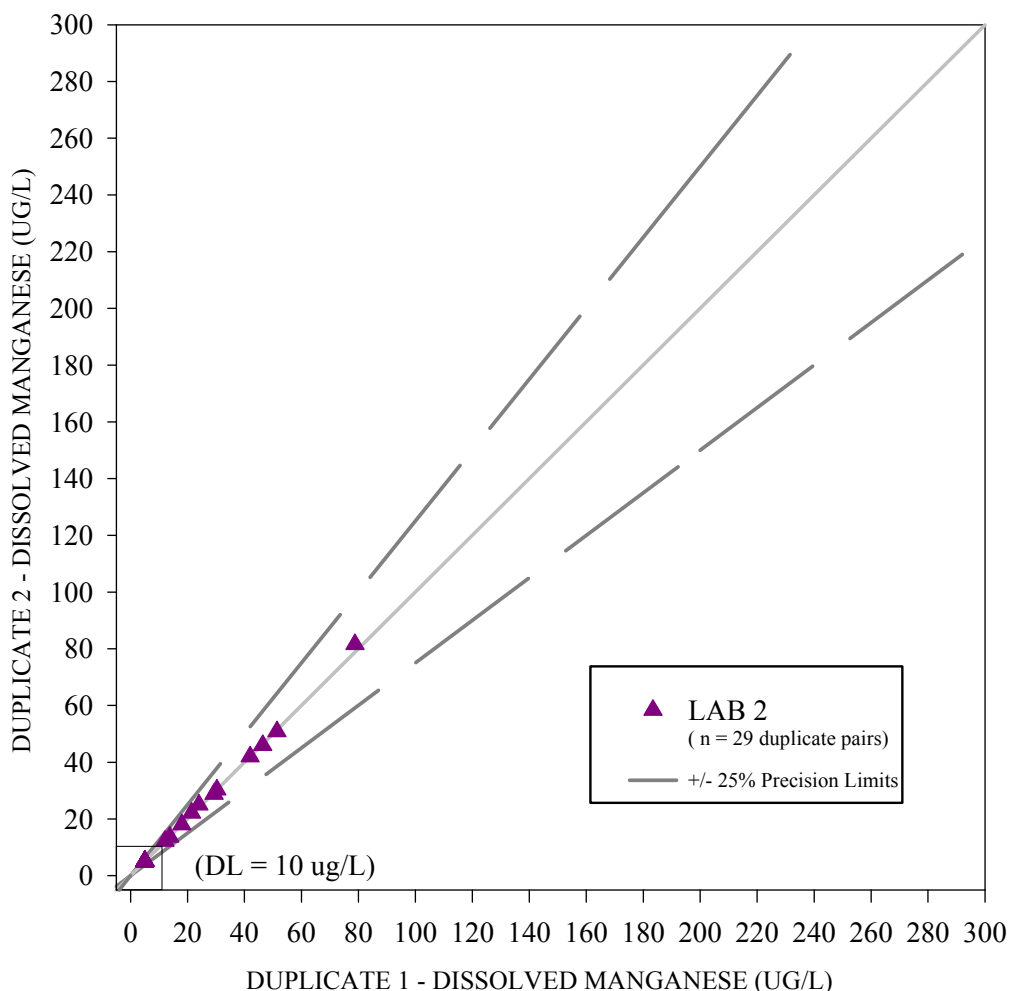
Figure Mn-2 plots the concentration of duplicate samples. The precision is only fair at the second lab. The values range up to about 25 times the detection limit.

Figure Mn-2. Comparison of Duplicates - Total Manganese - Lab 2 Only



Dissolved manganese was also measured in this study. Results of duplicate samples for dissolved manganese are plotted in Figure Mn-3. Precision is better than that for total manganese, but the range of concentration is smaller, being only about 8 times the detection limit.

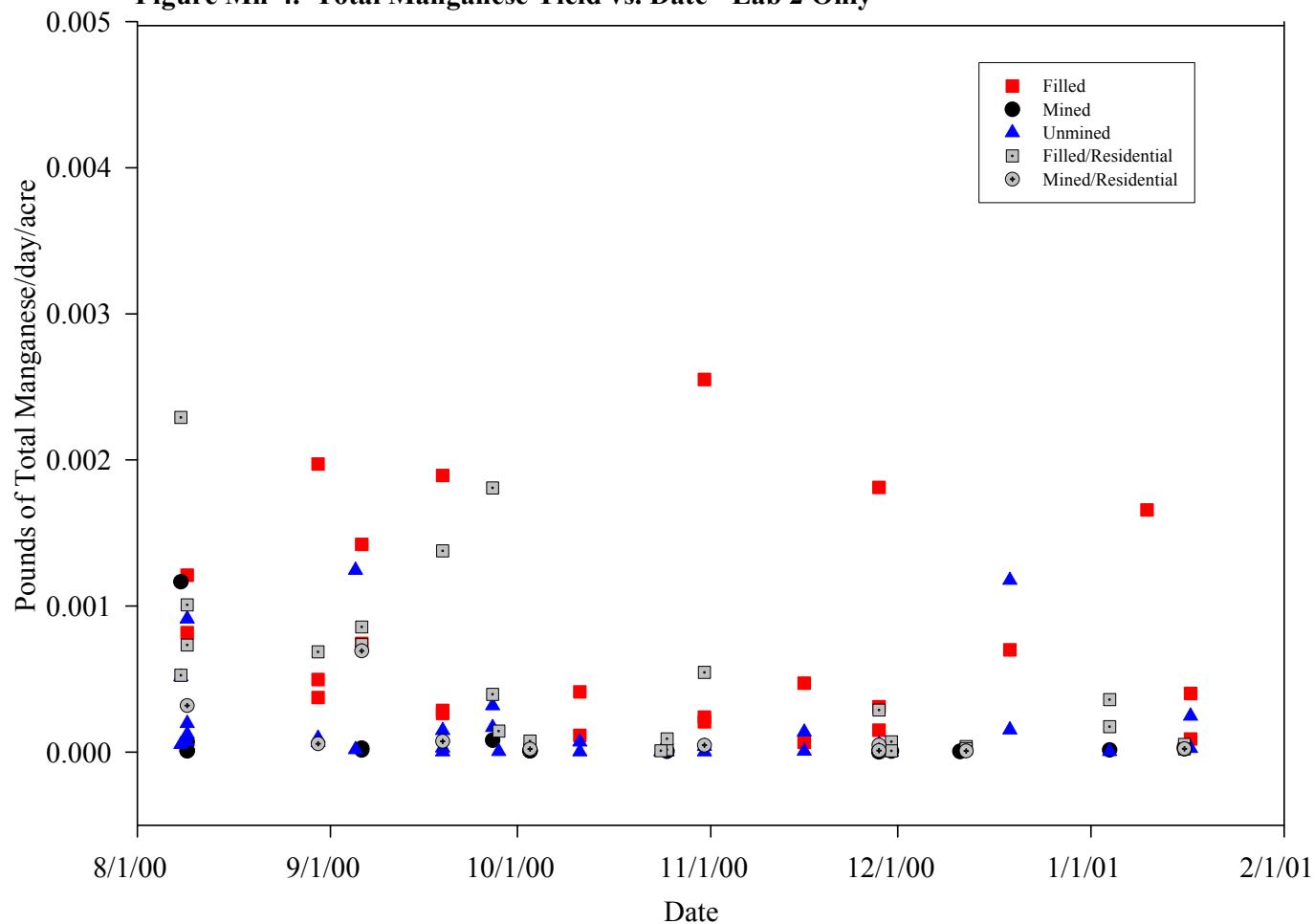
Figure Mn-3. Comparison of Duplicates - Dissolved Manganese - Lab 2 Only



The data for manganese indicate it occurs across the study area. MTM/VF mining can increase the concentration of manganese in streams and require long term chemical treatment of discharges. Careful analysis and special handling of mine overburden is required to minimize the concentration of manganese in permitted wastewater discharges from MTM/VF mines.

Yield rates for manganese are presented in Figure Mn-4 for the second laboratory only. Yield rates are all less than 0.003 pounds per acre per day and the higher values are from most categories of sites. This indicates that higher manganese values in streams are not closely related to mining activities and that mines are complying with permit limits on manganese.

Figure Mn-4. Total Manganese Yield vs. Date - Lab 2 Only



5.8 Specific Conductance Data

Specific conductance or conductivity is a quick method of measuring the ion concentration of water. The 18th Edition of *Standard Methods for the Examination of Water and Wastewater* states:

Conductivity is the measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions: on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

The unit of measure is micromhos per centimeter or in the International System of Units, millisiemens per meter. Specific conductance is measured in the field using a calibrated meter. The median conductance value of samples from site MT-24 was 2,856 while the median conductance of all samples at Unmined sites was 62.6 micromho/cm, indicating higher

concentrations of ions came from the area upstream of MT-24 site.

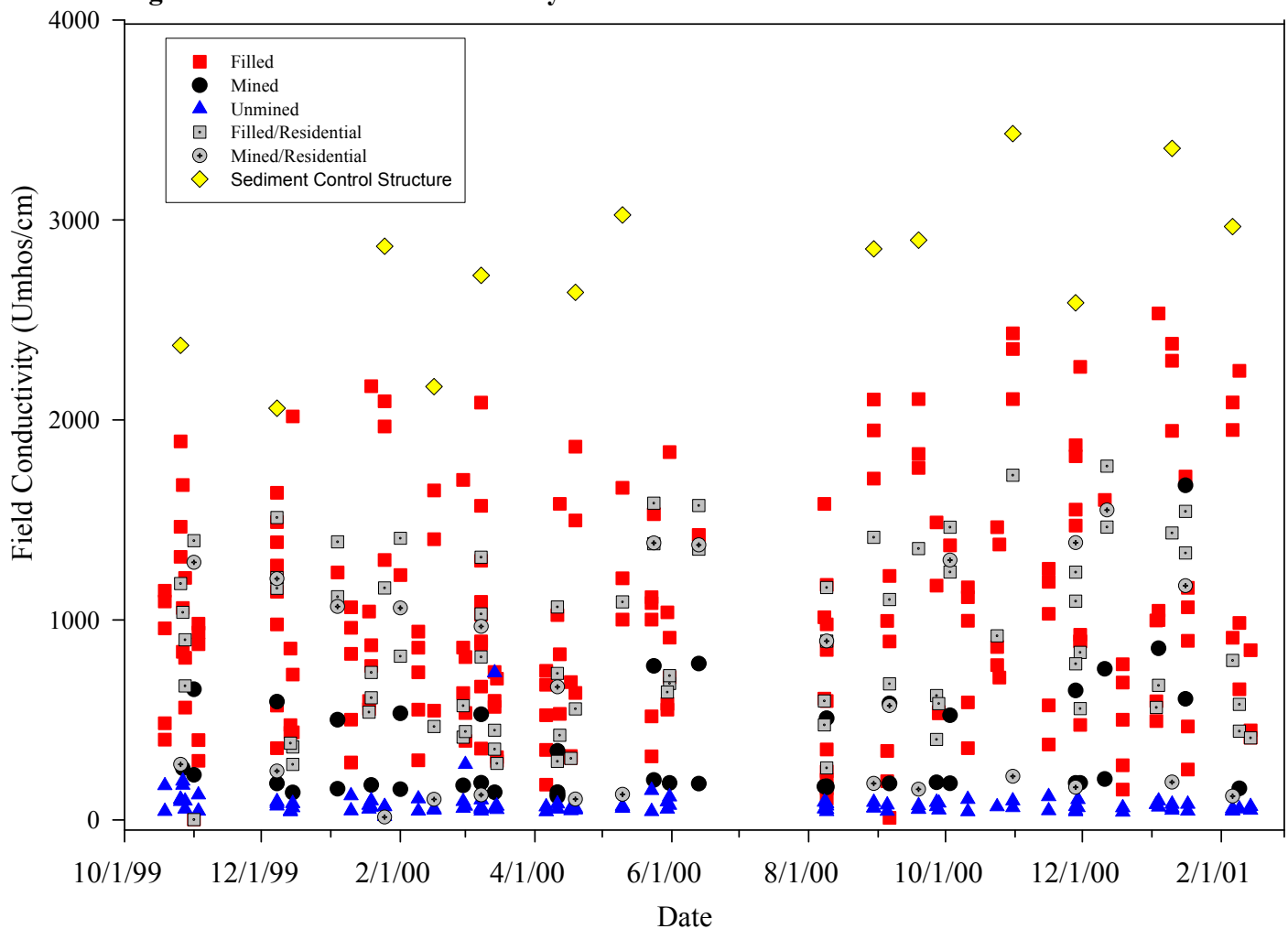
Although there is no stream criterion for conductivity in West Virginia, it is commonly measured as part of streams surveys. Regarding the impact of conductivity on fish and aquatic life, the California State Water Resources Control Board's *Water Quality Criteria* states:

.... Hart et al. have reported that among United States waters supporting a good fish fauna about 5 % have a specific conductivity under 50×10^{-6} mhos [50 micromhos/cm] at 25°C ; about 50 percent under 270×10^{-6} mhos [270 micromhos/cm]; and about 95 percent under 1100×10^{-6} mhos [1100 micromhos/cm].

The conductivity of the streams during the sampling event has been included in Figure Cond-1. A different symbol has been used for each category of site so evaluation of trends is more evident. Conductivity at Filled sites can be 100 times greater than that at Unmined sites. The highest values are consistently at the Sediment Control Structure (MT-24) which is on a reclaimed MTM/VF mine.

It is no surprise that MTM/VF operations increase the conductance of streams draining the disturbed areas. Figure Cond-2 plots the conductivity vs the normalized flow rate (the flow rate measured at the time of sampling divided by the drainage area for that site) for two categories of sites - Filled and Unmined. Unmined sites have a consistently low conductivity no matter what the flow. Filled sites have a broad range of conductivity much higher than Unmined sites indicating that MTM/VF mining increases specific conductance in streams. In larger drainage area sites it is common to have lower flows associated with higher conductivity. This is discussed at the end of this report under the topic Flow Rate Data.

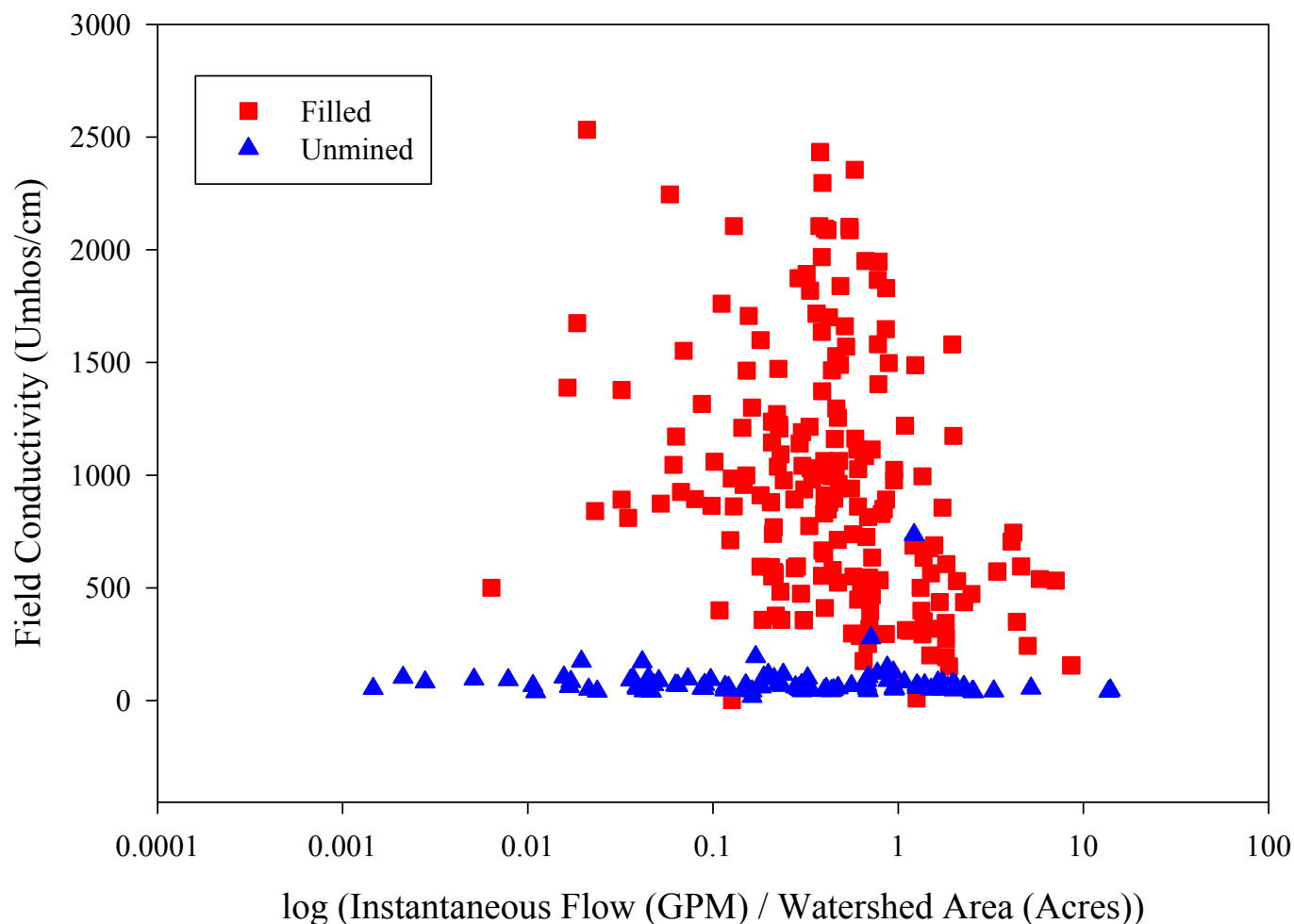
Figure Cond-1. Field Conductivity of All Sites vs. Date



5.9 Selenium Data

The selenium data indicate numerous violations of the West Virginia stream water quality criterion related to MTM/VF mining. Further discussion of selenium results is located in the

Figure Cond-2. Field Conductivity vs. Instantaneous Flow / Watershed Area



section of this report describing compliance with stream water quality criteria.

5.10 Alkalinity Data

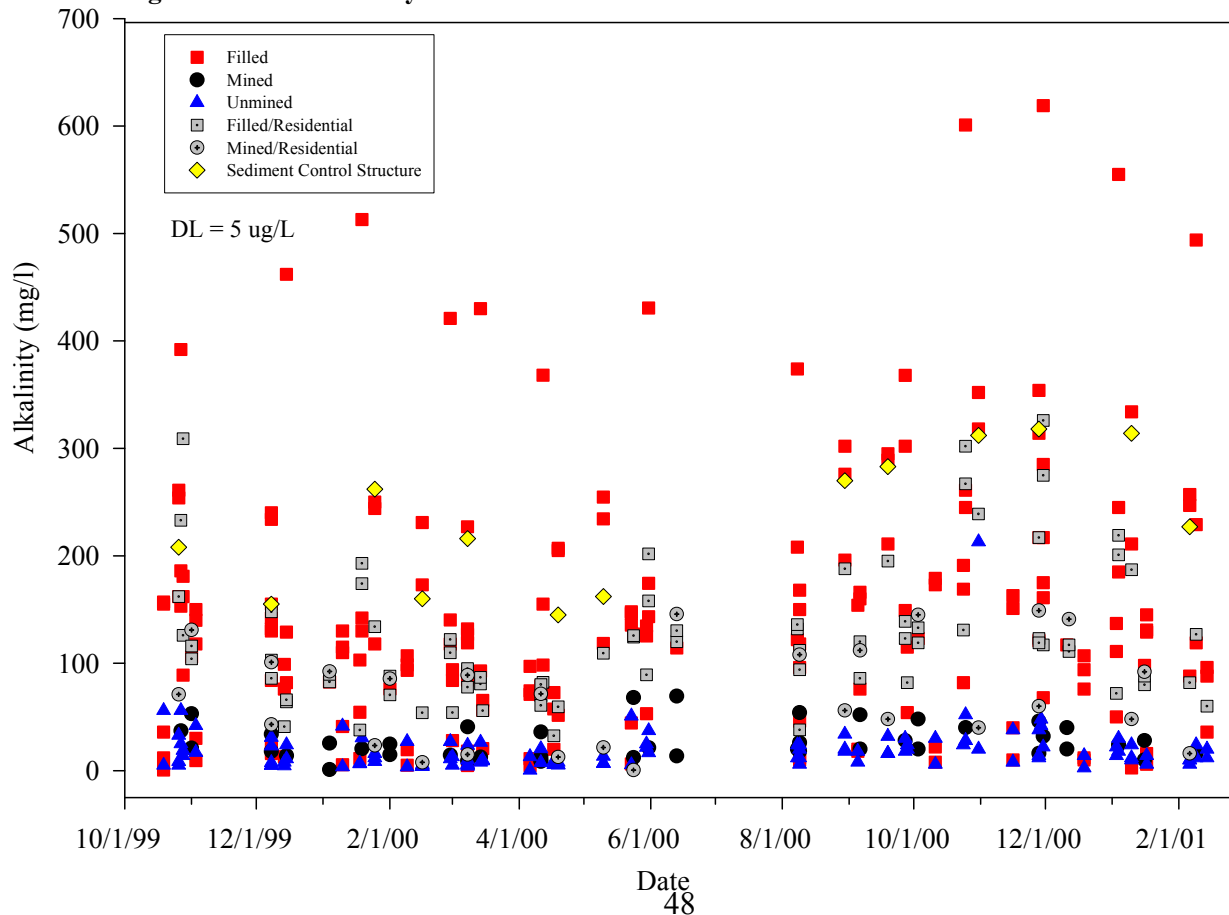
According to the 18th Edition of Standard Methods, alkalinity of a water is its acid-neutralizing capacity and is primarily a function of carbonate, bicarbonate, and hydroxide content. Alkalinity is not a specific substance but rather combination of substances. Regarding the impact of alkalinity on aquatic life, the California State Water Resources Control Board's *Water Quality Criteria* states:

It is generally recognized that the best waters for support of diversified aquatic life are those with pH values between 7 and 8, having a total alkalinity of 100 to 120 mg/L or more. This alkalinity serves as a buffer to help prevent any sudden change in pH value, which might cause death to fish or other aquatic life.

5.10.a Alkalinity Concentration in Stream Samples

The concentration of alkalinity in samples from all sites vs date are plotted in Figure Alk-1. The detection limit was 4 mg/L. Values for many Filled sites are several times higher than the Unmined sites. Twelve of the thirteen highest values are from site MT-34B and those concentrations are even higher than the values at the Sediment Control Structure which is on a reclaimed MTM/VF mine. The increase in alkalinity at a MTM/VF mine site is sometimes augmented by liming of areas being reclaimed to improve vegetation growth or by addition of alkaline materials during the mining process to line ditches to neutralize acidic materials. There are also some chemical treatment facilities upstream of some sites. These facilities usually add excess alkalinity as they neutralize acid mine drainage or remove manganese to comply with

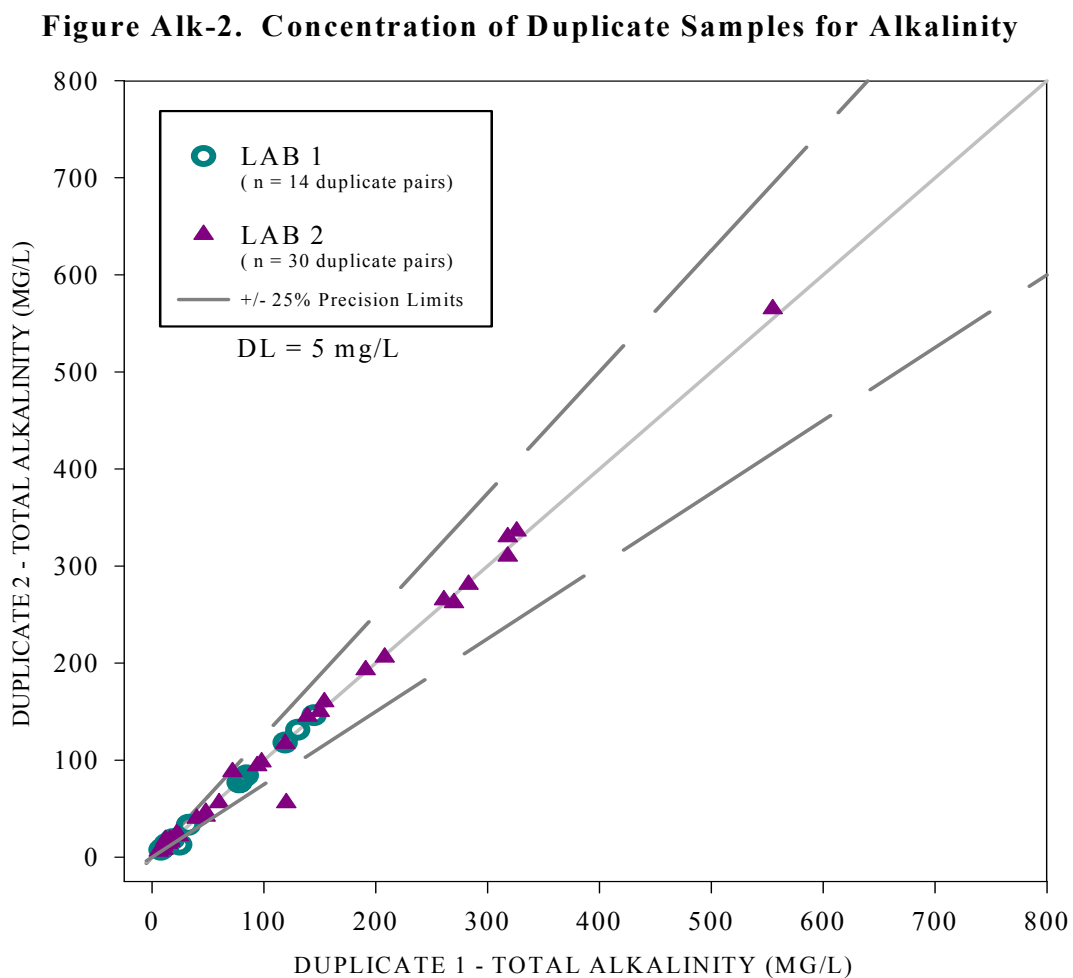
Figure Alk-1. Alkalinity Concentration for All Sites vs. Date



permit limits on discharges. These factors also influence other parameters like specific conductance, dissolved solids, and hardness.

5.10.b QA Samples for Alkalinity

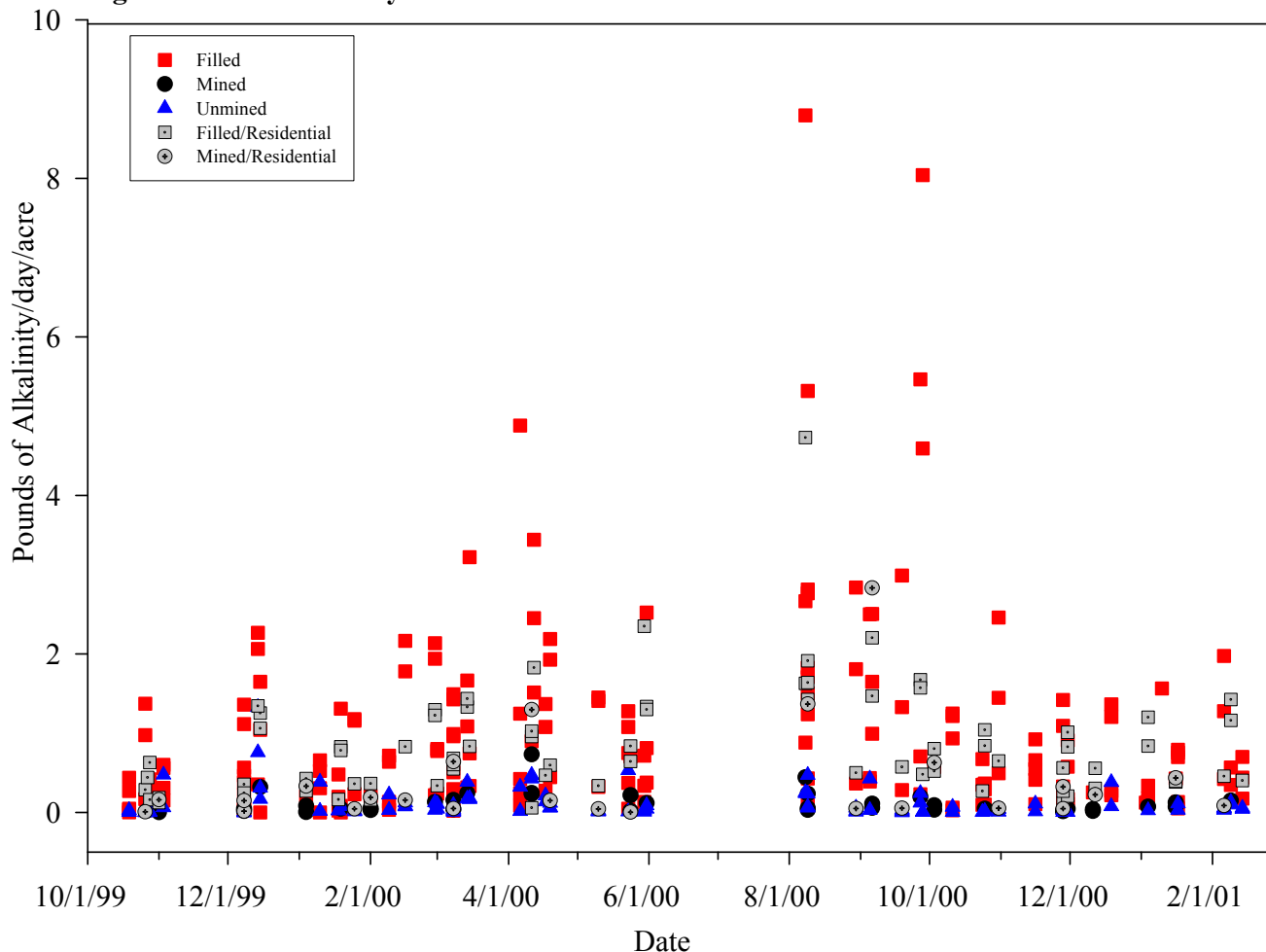
Figure Alk-2 presents a plot of the concentration of duplicate samples. Data from both laboratories is precise over a range from the detection limit of 5 ug/L to a maximum of 600 mg/L



5.10.c Alkalinity Yield

Figure Alk-3 plots the Yield of alkalinity

Figure Alk-3. Alkalinity Yield for All Sites vs. Date



for all samples. Yield rates for Unmined sites are less than 1 pound per day per acre while Yield rates at Filled sites range to 5 pounds per day per acre. There appears to be a slight decrease in alkalinity yield during fall and winter months. The highest yield was at MT-34B in August 2000. Other high yield values are from various sites scattered across the study area.

5.11 Potassium Data

The California State Water Resources Control Board's *Water Quality Criteria* reports that potassium is a common element constituting 2.4 percent of the earth's crust. Potassium salts are extremely soluble and can usually only be removed from water through evaporation. Potassium is an essential nutritional element for humans but acts as a cathartic in concentrations greater than 2000 mg/L. Regarding impacts to fish and other aquatic life, the report states:

The toxicity of potassium to fish is reduced by calcium, and, to a lesser degree, by sodium. Potassium is more toxic to fish and shellfish than calcium, magnesium, or sodium. ... Several investigators found, independently, that potassium could be toxic to fish in soft or distilled waters at concentrations of 50-200 mg/L

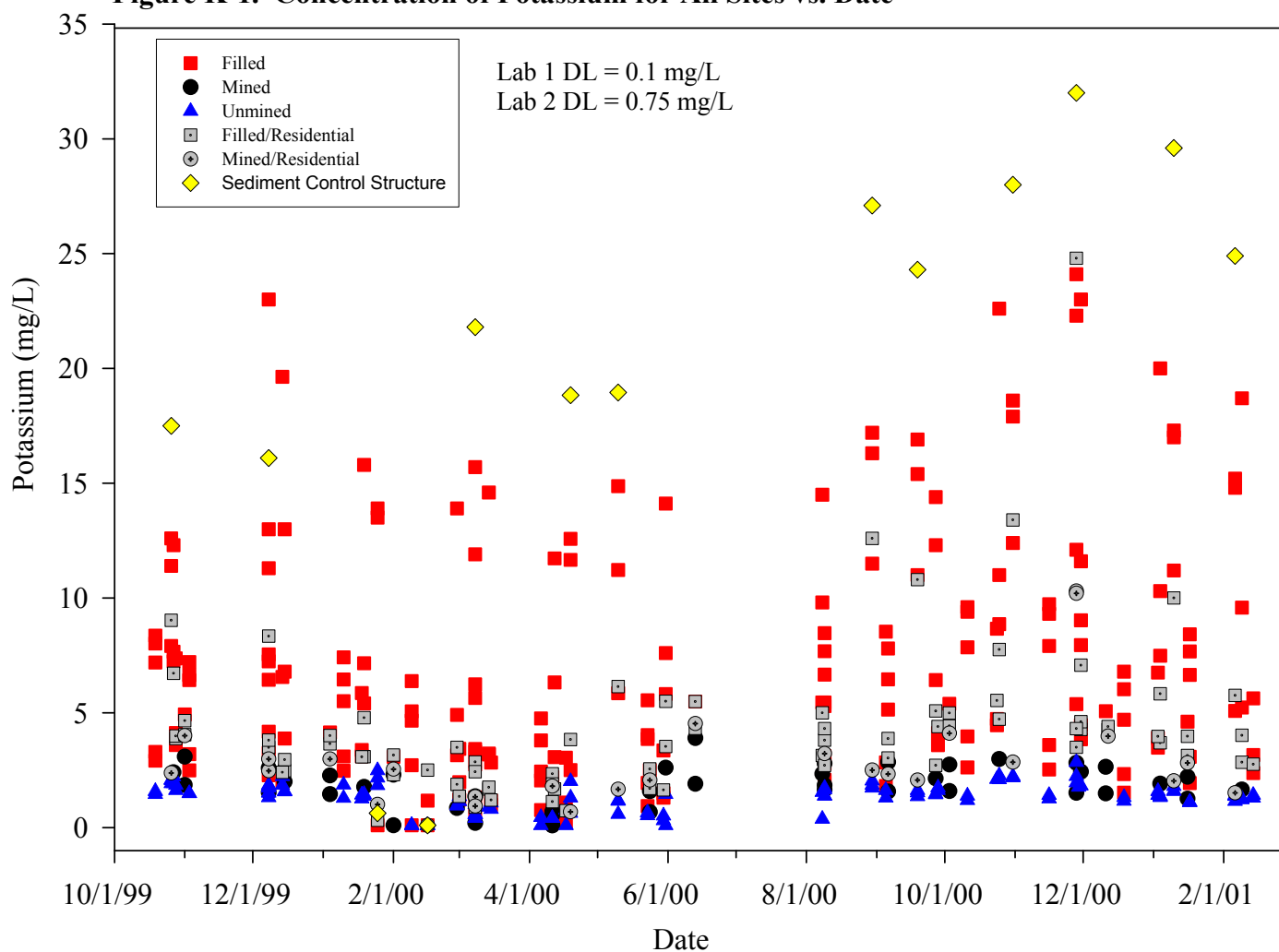
Potassium is a component of many fertilizers which are sometimes applied to mined areas to stimulate vegetation growth. This practice could be augmenting the increase of potassium in streams below mine sites being reclaimed.

5.11.a Potassium Concentration in Stream Samples

Figure K-1 shows the concentration of potassium in samples from all sites vs date. The detection limit was 0.1 mg/L for Laboratory 1 and 0.75 mg/L for Laboratory 2. The potassium data from both laboratories passed the QA review with only two samples being rejected and those were at Laboratory 1.

The higher concentrations are consistently at sites in the Filled category indicating that MTM/VF

Figure K-1. Concentration of Potassium for All Sites vs. Date

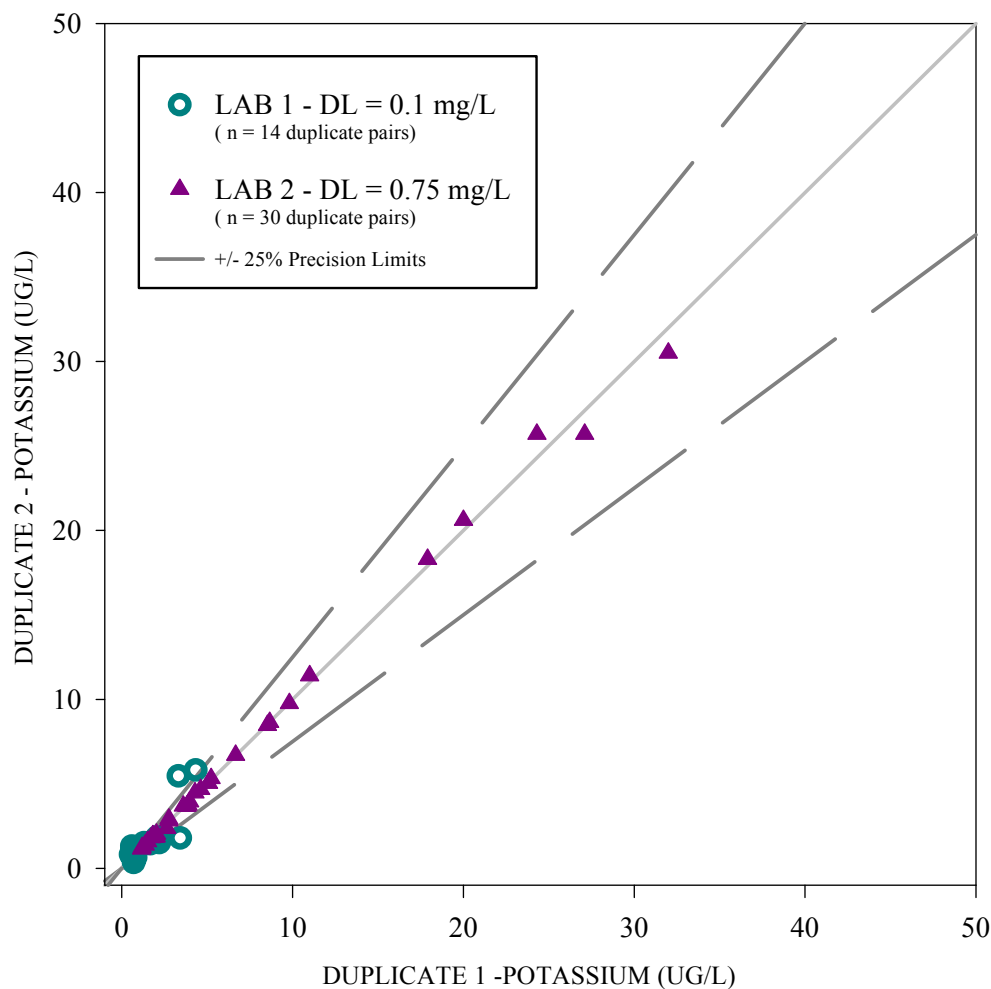


mining operations increase the concentration of potassium in streams. There are 40 values above 10 mg/L and 29 of those are in the Mud River, 10 in the Spruce Fork, and one in the Clear Fork watersheds. All sites in the Unmined category have low concentrations of potassium.

5.11.b QA Samples for Potassium

Figure K-2 plots the concentration of potassium in all duplicate samples collected during this study. The plot indicates the data are more precise at the second laboratory over the range of concentrations from the detection limit to about 30 mg/L.

Figure K-2. Comparison of Duplicate Samples - Potassium

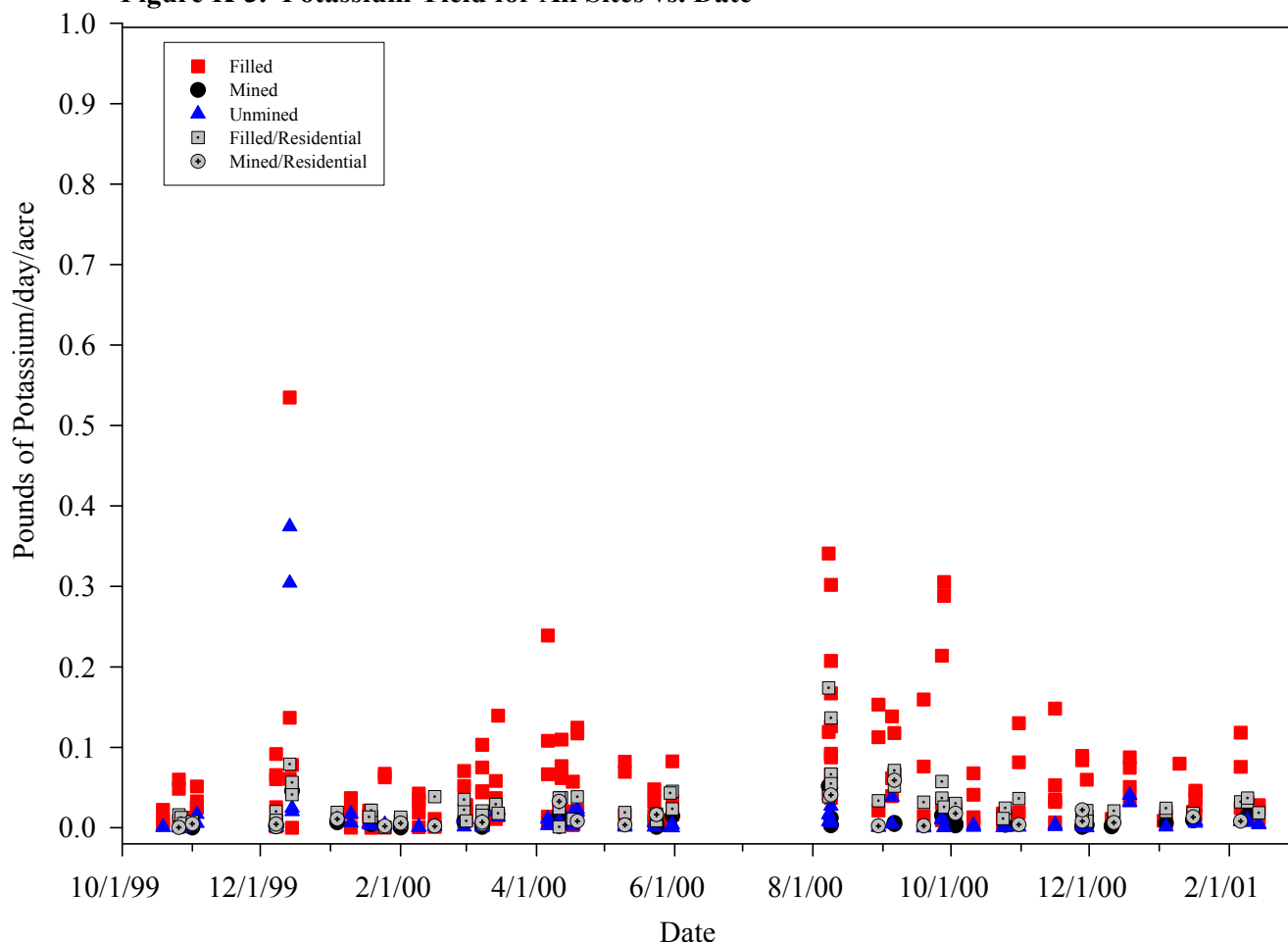


5.11.c Potassium Yield

Figure K-3 plots the Yield of potassium for samples from all sites vs date. The data would indicate that potassium Yield rates are generally below 1 pound per day per acre, but the higher values are usually from sites in the Filled category. The three higher yield values for samples collected in December 1999 are all in the same watershed. They are sites MT-50, 51, and 52. The yield rates are believed to be elevated on this occasion due to recent rains. The note on the field sheet states “Heavy precipitation in the last 24 hours.” None of the higher concentrations for the December 1999 samples were from these three sites so the increase in flow rates resulted in higher yield rates.

5.12 Sodium Data

Figure K-3. Potassium Yield for All Sites vs. Date



The California State Water Resources Control Board’s *Water Quality Criteria* states:

This very active metal does not occur free in nature, but sodium compounds constitute 2.83 percent of the crust of the earth. Owing to the fact that most sodium salts are extremely soluble in water, any sodium that is leached from soil or discharged by industrial wastes will remain in solution.

Regarding the impact on fish and aquatic life, the report states:

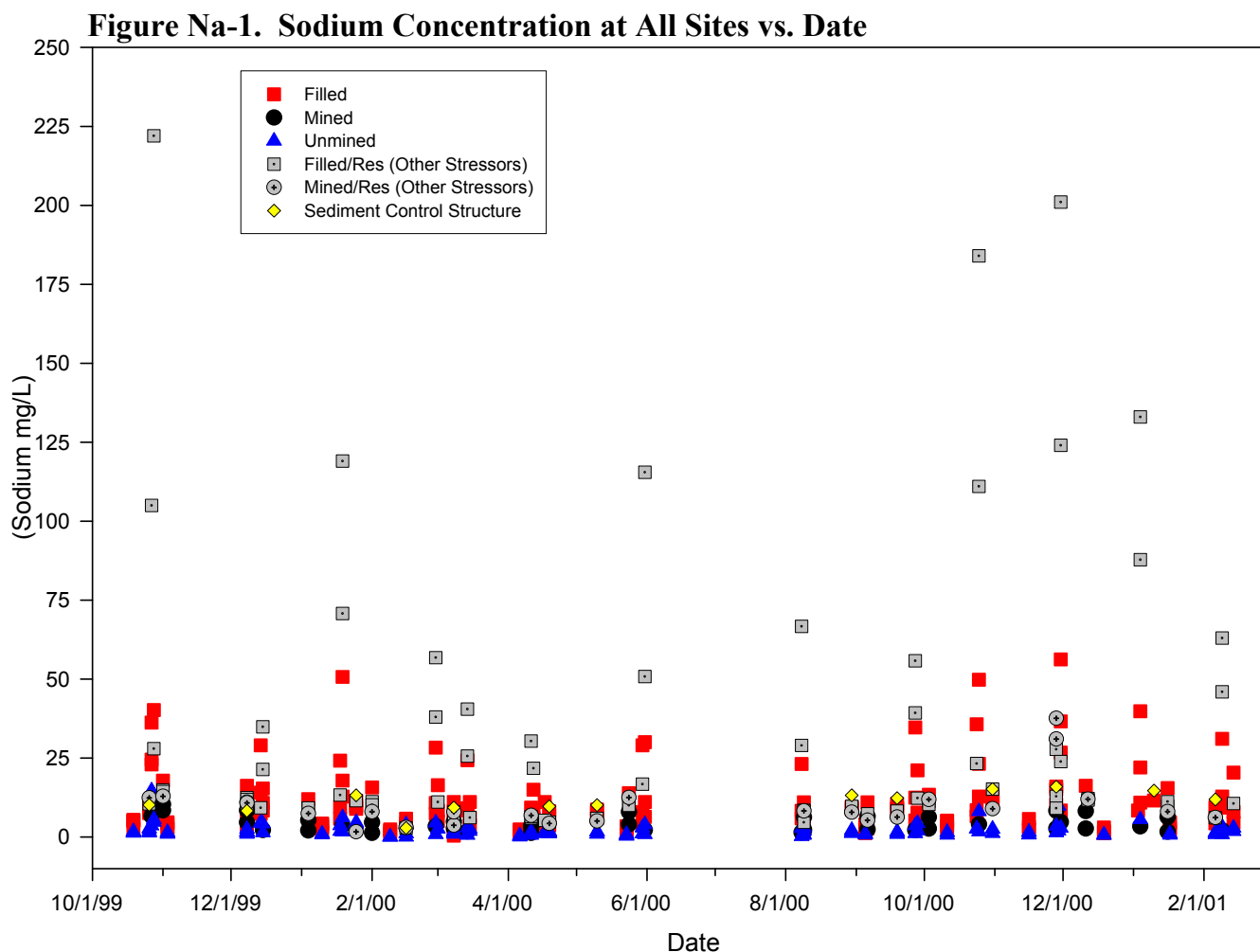
Of the United States waters supporting good fish fauna, ordinarily the concentration of sodium plus potassium is less than 6 mg/L in about 5 percent; less than 10 mg/L in about 50 percent; and less than 85 mg/L in about 95 percent.

5.12.a Sodium Concentration in Stream Samples

Sodium concentrations for all sites are plotted in Figure Na-1. The detection limit was 1 mg/L. The highest values are for sites in the category Filled/Residences and occurred in the Spruce Fork watershed at sites MT-40 and MT-48. MT-40 is downstream of 7 MTM/VF mine permits and 3 refuse piles while MT-48 is below four communities. Possible sources of sodium would be mine drainage treatment facilities using sodium hydroxide and winter time salting of highways.

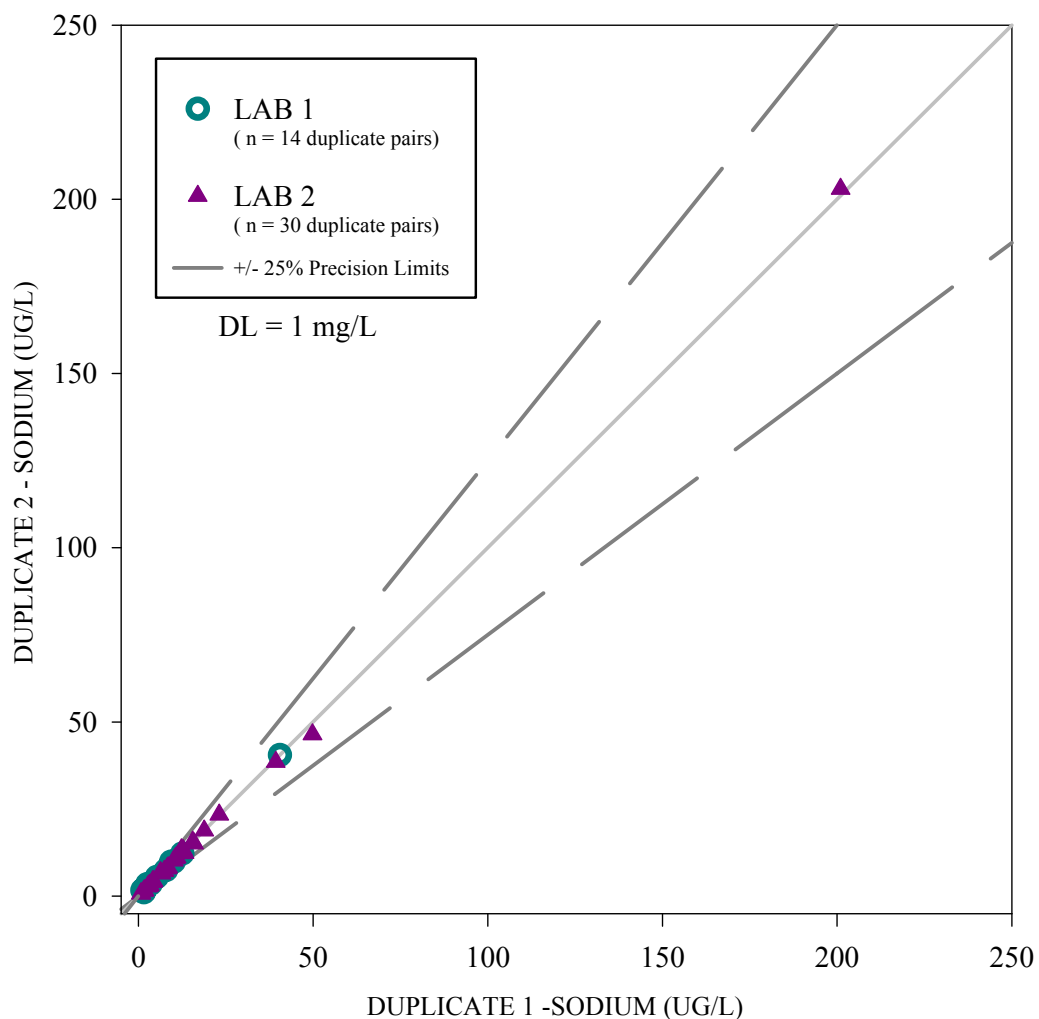
5.12 c QA Samples for Sodium

The results of duplicate samples are plotted in Figure Na-2. The detection limit was 1 mg/L. The



data are very precise with multiple values below about 60 mg/L. The one value at slightly over 200 mg/L also is very precise. Both laboratories have good precision for this parameter.

Figure Na-2. Sodium Concentration of Duplicate Samples

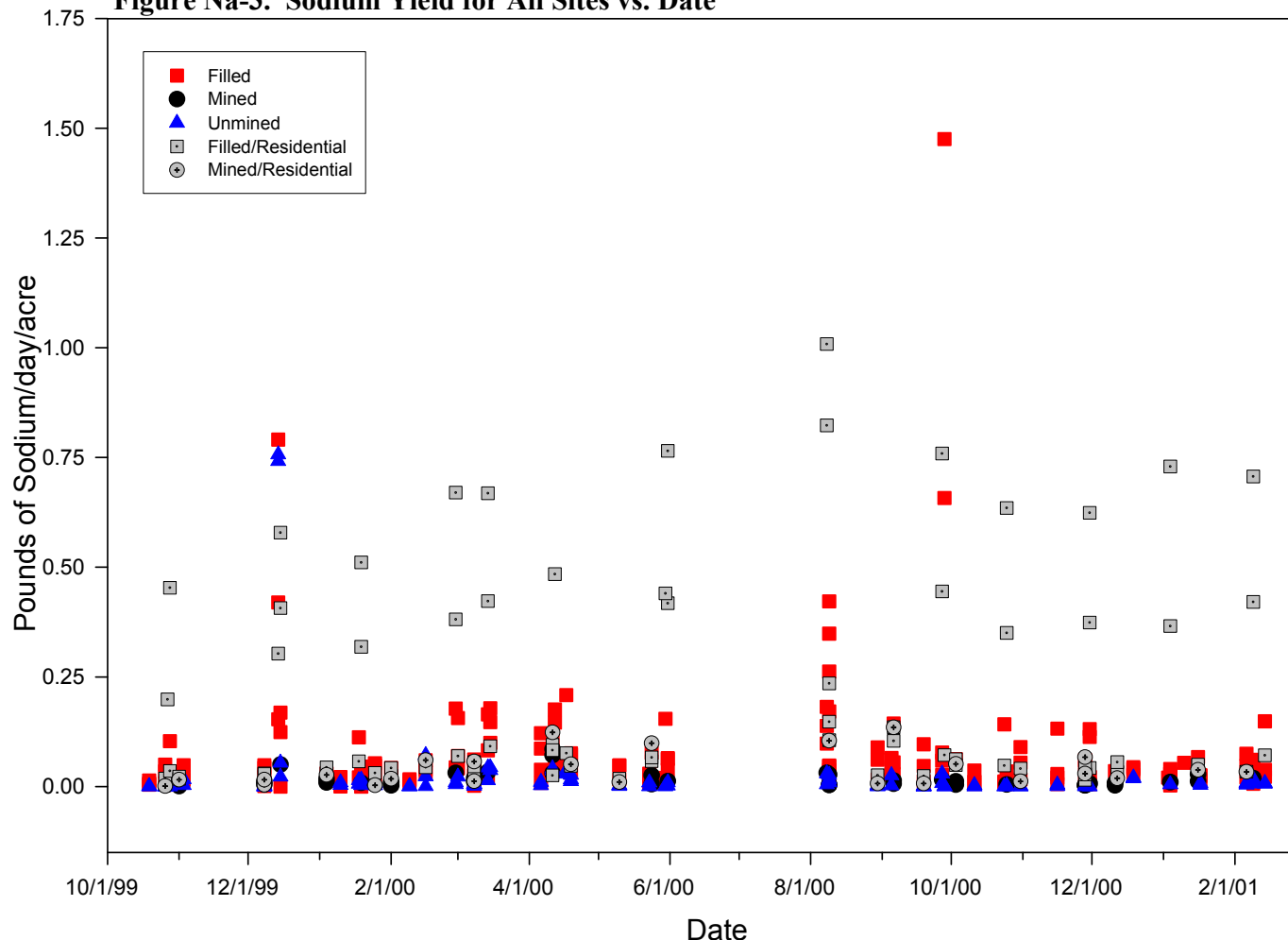


5.12.c Sodium Yield

Yield rates for sodium are plotted in Figure Na-3. Most values are less than 0.25

pounds per day per acre. The higher values at the Filled/Residence sties were noted in Figure Na-1 also and are possible related to use of road salt or the use of sodium hydroxide in chemical treatment facilities at mine discharges. There are higher values on two sample occasions - December 1999 and September 2000. The three values near 0.75 pounds per day per acre in December 1999 were at MT-50, 51, and 52. The field sheet not for those samples noted "Heavy precipitation in the last 24 hours." The higher yield rates for the Filled/ Residential sites is for MT-40 and MT-48, which correspond to the higher concentrations listed earlier in Figure Na-1 showing concentrations vs date. The highest yield of 1.5 pounds per day per acre is at site MT-60. The flow rate for that sample was the highest recorded for that site during this study while the

Figure Na-3. Sodium Yield for All Sites vs. Date



concentration was 21.1 mg/L, below the average for that site (30.5 mg/L). There were no comments on the field sheet indicating anything unusual.

5.13 Chloride Data

Chloride is one of the parameters limited by WVDEP water quality criteria and is discussed later in the report under that topic.

5.14 Acidity Data

Acidity, like alkalinity is not a specific chemical but instead is a measure of the effects of a combination of substances and conditions in the water. Waters can have both acidity and alkalinity values at the same time. Acidity may be present from natural causes and from human activity. Acid waters are sometimes formed as a result of mining activity, especially in sulfur bearing formations. Regulations have sought to address concerns with excess acidity resulting

from mining activities through the permitting processes. There are elaborate regulations which focus on determining and minimizing the potential for forming acid waters. There are also effluent limits on the pH (discussed later in this report) of discharges.

Acidity was detected in 20 % of the 399 samples that passed the QA/QC review. The second laboratory found acidity in 31 samples above the detection limit of 2 mg/L. Twenty of these detected values came from sites in the Filled category. The site with the highest concentrations of acidity was MT-34B, a site in the Filled category with an active mine upstream. Five of the 31 values came from this site and they ranged from 29 mg/L to 40 mg/L. However, there were no violations of the stream limits on pH at this site. The only violations of the stream criteria for pH detected were at Unmined sites.

Acidity in streams can be increased by MTM/VF mining but mine permitting activities address this potential problem.

5.15 Nitrate and Nitrite Data

The *Water Quality Criteria, 1972* “Blue Book” discusses Nitrate-Nitrite in water supplies and notes that chlorination converts the nitrite to nitrate. They make the following recommendation concerning nitrate in water:

On the basis of adverse physiological effects on infants and because the defined treatment process has no effect on the removal of nitrate, it is recommended that the nitrate-nitrogen concentration in public water supply sources not exceed 10 mg/L. On the basis of its high toxicity and more pronounced effect than nitrate, it is recommended that the nitrite-nitrogen concentration in public water supply sources not exceed 1 mg/L.

The California State Water Resources Control Board’s *Water Quality Criteria* also discusses nitrate and nitrite and notes that nitrites are often formed in streams by the natural degradation of ammonia and organic nitrogen. Since they are usually quickly oxidized to nitrates, they are seldom present in surface waters in significant concentrations. The presence of nitrates and nitrites usually indicates an organic loading source such as sewage or fertilizer. Regarding the impact on fish and other aquatic life, the report states:

High nitrate concentrations in effluents and water stimulate the growth of plankton and aquatic weeds. By increasing plankton growth and the development of fish food organisms, nitrates indirectly foster increased fish production. Hart et al. report references to the effect that United States waters supporting a good fish life ordinarily 5 percent have less than 0.2 mg/L of nitrates; 50 percent have less than 0.9 mg/L; and 95 percent have less than 4.2 mg/L.

5.15.a Nitrate-Nitrite Concentration in Stream Samples

The laboratory data for nitrate and nitrite is somewhat confusing and of mixed quality, partly due to changes in what parameters were being measured. The first laboratory began this survey analyzing for nitrates and nitrites separately but it was soon evident that the 48 hour holding time was difficult to meet. The parameter was switched to nitrate - nitrite (nitrogen) which has a 28 day holding time for the contract with the second laboratory. The data from the first laboratory was often rejected for holding time violations and only 54 % of the nitrate samples and 66% of the nitrite samples passed the QA review. The second laboratory began testing for nitrate and nitrite separately but soon switched to nitrate plus nitrite as nitrogen. The first samples at the second laboratory were manually converted to nitrate plus nitrite as nitrogen values and entered into the database. Overall 94 % of the data from the second laboratory for nitrate plus nitrite as nitrogen passed the QA/QC review. The detection limit was 0.1 mg/L. The highest value detected at the second laboratory was 23.4 mg/L at site MT-18, a site in the Filled category, on 01/10/00. Some high values might be caused by careless handling of the nitrogen compound explosives used at surface mines or when nitrogen containing fertilizers are spread on surface mines to encourage growth of vegetative cover during reclamation, but it is not known if this might be part of the cause for this elevated value. Many samples had no detectable concentrations and they were in all categories of sites. The Unmined site with the most detectable concentrations and the highest values (second lab data only) was MT-95 in the Twentymile Creek watershed. Nitrate plus nitrite as nitrogen values ranged from 0.73 mg/L to 1.1 mg/L in each of the six samples from the site.

MTM/VF mining operations can increase the concentration of nitrate plus nitrite as nitrogen in streams.

5.16 Parameters Present in Low Concentrations

5.16.a Total Phosphorous

Phosphorous was detected in only one of 213 samples at the second laboratory. The concentration was 0.12 mg/L. No samples were rejected in the QA/QC review. Since the detection limit was 0.10 mg/L, this would indicate that stream concentrations of phosphorous are not being measurably impacted by MTM/VF mining.

5.16.b Total Copper, Lead and Nickel

Copper, lead, and nickel were usually below the detection limit for all samples tested at the second laboratory but several samples had detectable concentrations as listed below. The only obvious pattern observed in the data is that many of the detections were in the Mud River watershed (MT-01 through MT-24). Site MT-24, a site on a reclaimed MTM/VF mine, had three measurable values of copper, all near the detection limit, no nickel values, and six of the eight detections for nickel. There is no clear indication that MTM/VF mining caused any changes in these metal concentrations in streams.

Site ID	Category	Date	Copper (DL = 5 ug/L)	Lead (DL = 2 ug/L)	Nickel (DL= 20 ug/L)
MT-01	Min/Res	01/10/01	10.3	ND	ND

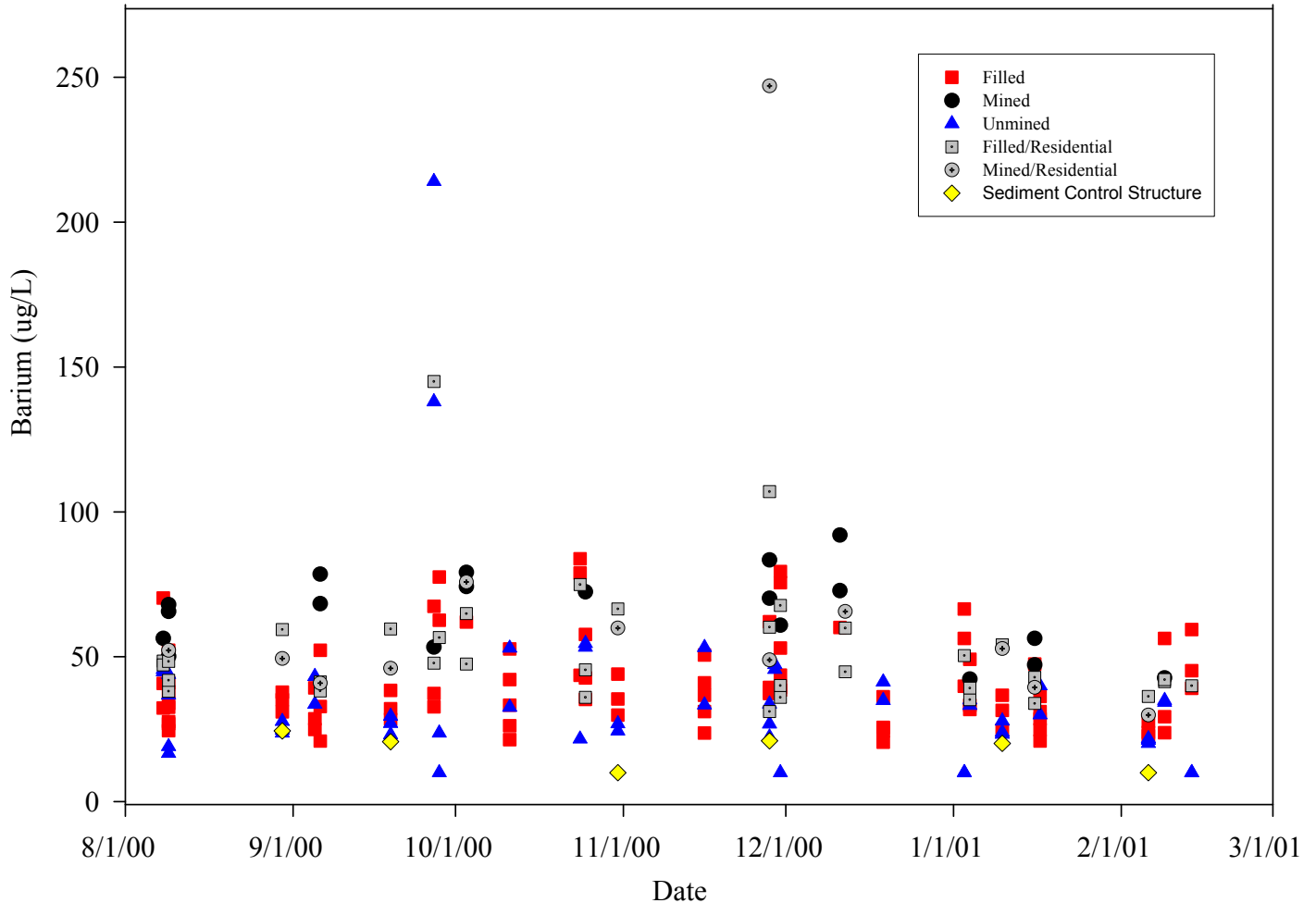
MT-13	Unmined	11/28/00	14.8	3.76	ND
MT-14	Filled	08/30/00	7.64	2.14	ND
MT-18	Filled	08/30/00	7.41	ND	ND
MT-23	Fill/Res	08/30/00 11/28/00	20.4 5.6	2.1 ND	ND ND
MT-24	Sediment Control Structure	08/30/00 09/19/00 10/31/00 11/28/00 01/10/01 02/06/01	8.15 ND 6.56 5.83 ND ND	ND ND ND ND ND ND	35.5 36.8 71.8 63.4 115 80.4
MT-39	Unmined	11/29/00	5.23	7.4	ND
MT-50	Unmined	08/09/00	ND	4.48	ND
MT-57B	Filled	08/09/00	ND	16.2	ND
MT-62	Fill/Res	09/06/00	ND	ND	37.6
MT-64	Filled	09/06/00	ND	ND	39.5
MT-69	Min/Res	11/28/00	6.72	ND	ND
MT-79	Mined	11/28/00 01/16/01	8.01 5.23	ND ND	ND ND
MT-81	Mined	11/28/00	ND	13.8	ND

5.17 Other Parameters Detected in Measurable Concentrations

5.17.a Total Barium

Barium was detected in 96 % of the 213 samples analyzed at the second laboratory. The detection limit was 20 ug/L. Concentrations are plotted in Figure Ba-1. They range to 250 ug/L but most values are below 75 ug/L. There were higher values on 9/27/00 and 11/28/00. The three samples in September were from MT-39 (138 ug/L), MT-40 (145 ug/L) and MT-42 (214 ug/L), all in the Spruce Fork watershed. Each concentration was two to three times the average for each site and flows were higher than average as well. A note on the field sheets for that day stated, “Recent heavy rains have changed the stream bottom ...” Sites MT-39 and 42 are both Unmined. The data would indicate there was a temporary release of barium in these two tributary watersheds and in fact the decreasing concentration of barium at downstream site MT-48 (47.8 ug/L) would also fit that theory. Barium muds are used in drilling for oil and gas. The highest concentration at any site was detected 11/28/00 at site MT-01 (214 ug/L) in the headwaters of the Mud River. The next site downstream on the Mud, MT-23 also had a higher than normal concentration of barium area. (107ug/L). This appears to be another instance of a temporary release of barium in a headwater area.

Figure Ba-1. Concentration of Barium for All Sites vs. Date - Lab 2 Only



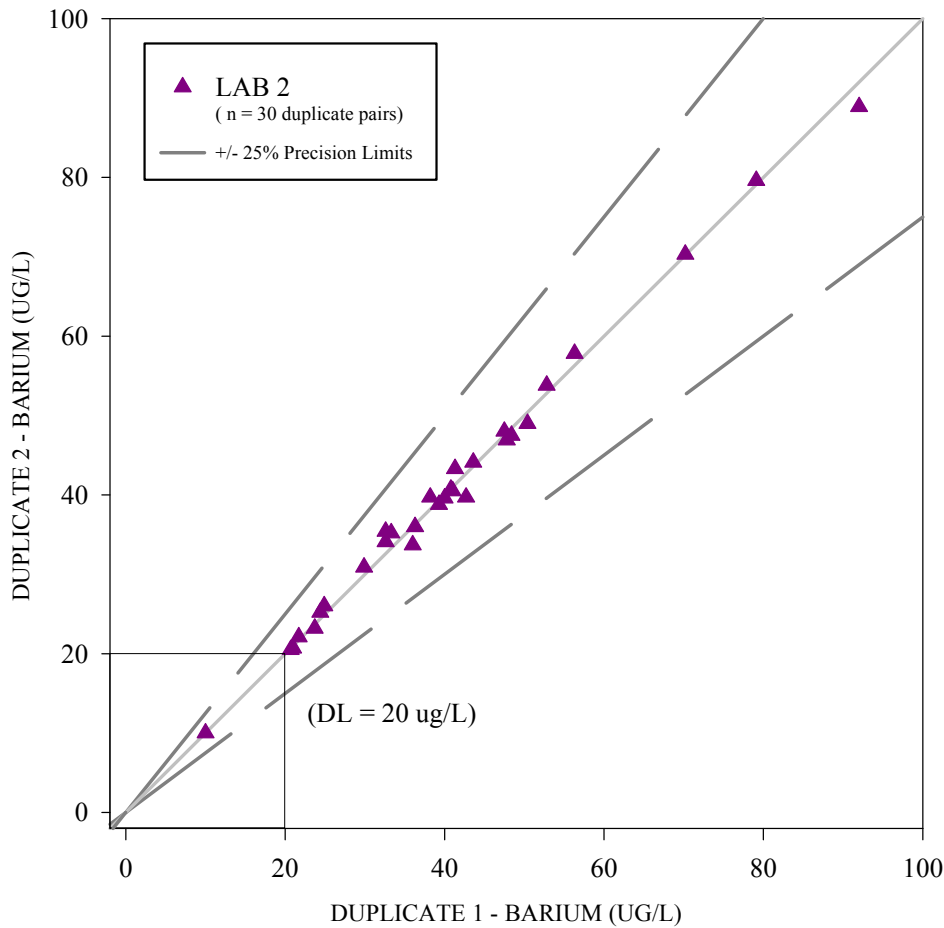
The only field note the crew made for that set of samples was for site MT-23 where they stated, "Beaverdam constructed downstream affecting depth and velocity flow measurements."

The mix of categories of sites across the range of concentrations and over the study period have no obvious patterns. Some Unmined sites have an elevated barium concentration while the sediment control structure and some Filled sites consistently have low concentrations of barium.

Duplicate sample results are presented in Figure Ba-2. The data indicate excellent precision to roughly 100 ug/L (five times the detection limit).

There is no clear indication that MTM/VF mining changes the concentration of barium in streams.

Figure Ba-2. Comparison of Duplicate Samples - Barium - Lab 2 Only



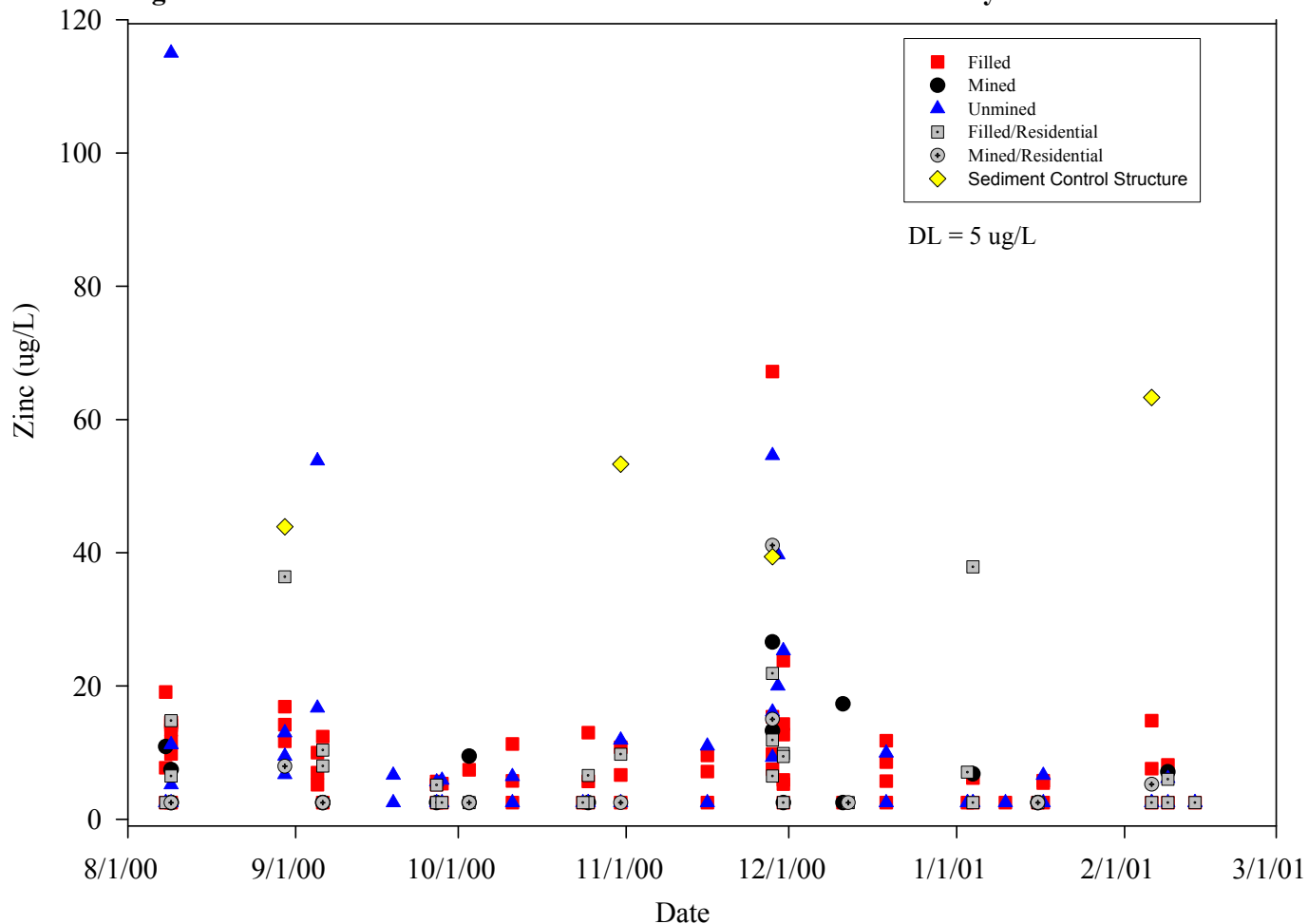
5.17.b Total Zinc

Zinc was detected in 51 % of the 199 samples that passed the QA/QC review and were analyzed in the second laboratory. The detection limit was 10 ug/L. The values are presented in Figure Zn-1.

Most values are below 20 ug/L where there was less precision in laboratory results. Zinc concentrations were elevated at MT-24, the Sediment Control Structure indicating that MTM/VF mining could cause elevated levels of zinc in streams, however there are also high values for zinc at four different Unmined sites (MT-50 on 8/9/00, MT-95 on 9/5/00, MT-13 on 11/28/00 and MT-39 on 11/29/00).

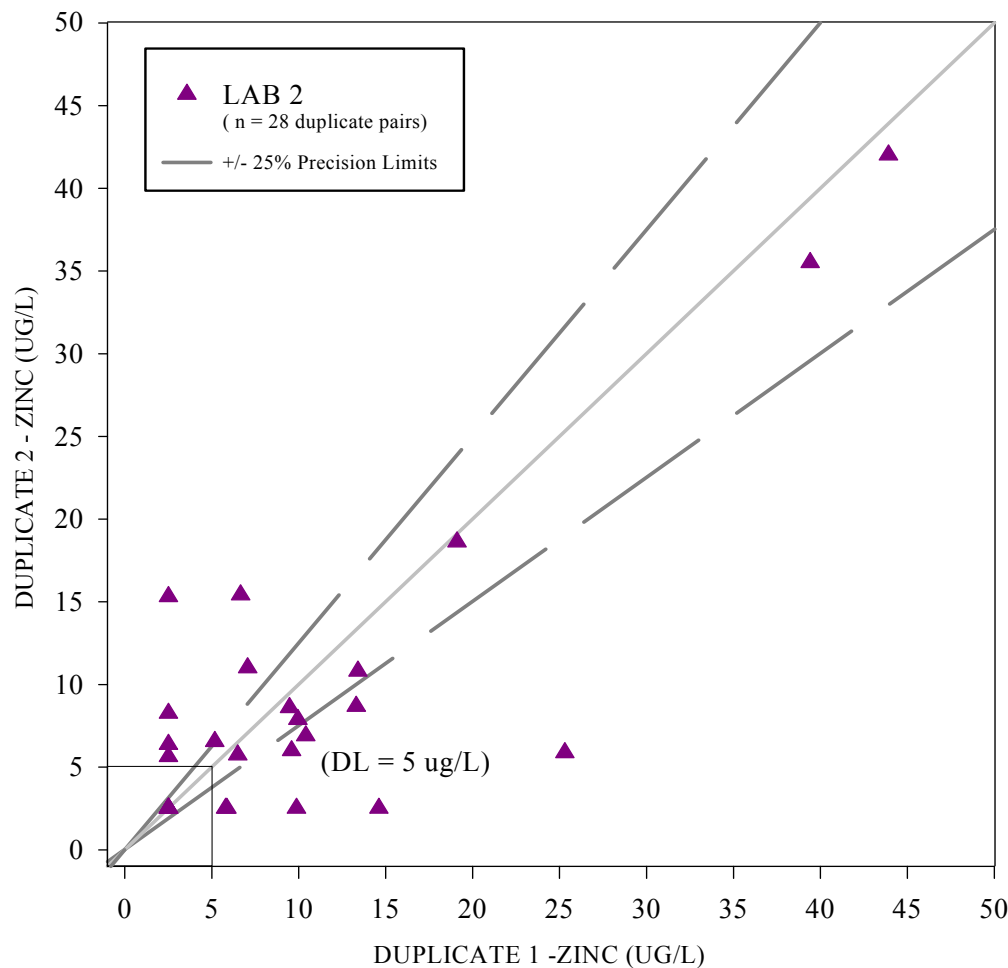
Duplicate sample results are presented in Figure Zn-2. The data indicate there were precision problems below a concentration of roughly 25 ug/L. Duplicate sample values range to roughly 45 ug/L which is 4.5 times the detection limit. Since most of the values from sites were below 25

Figure Zn-1. Concentration of Zinc for All Sites vs. Date - Lab 2 Only



ug/L where there was less precision, there is no clear indication that MTM/VF mining changes the concentration of zinc in streams.

Figure Zn-2. Comparison of Duplicate Samples - Zinc - Lab 2 Only



5.17.c Total Organic Carbon & Dissolved Organic Carbon

TOC and DOC results were generally very low near the detection limit of 1 mg/L. There was a confounding factor with the DOC test in that something appeared to be leaching from the filter used to remove the suspended matter in the field. The field crews used 45micron cellulose acetate membrane disposable sterile syringe filters. Whatever this interfering material was, it would create an organic value of up to 2 mg/L in some samples resulting in QA/QC flags on data. Of the 213 samples collected, 180 TOC values passed the QA/QC review and 170 DOC samples passed. TOC was detected in 77 % of the samples and DOC was detected in 86 % of the samples passing QA/QC review.

Figure TOC-1 plots the results of duplicate samples for TOC at the second laboratory. It illustrates the lack of precision in concentrations below about 2.5 mg/L. The range of duplicate sample values went to 3 mg/L. The maximum concentration of TOC recorded at the second laboratory was 4.4 mg/L. Only 14 (10%) of the 138 values detected were above 2.5 mg/L. Four of the 14 were at Unmined sites.

Figure TOC-1. Comparison of Duplicate Samples - Total Organic Carbon - Lab 2 Only

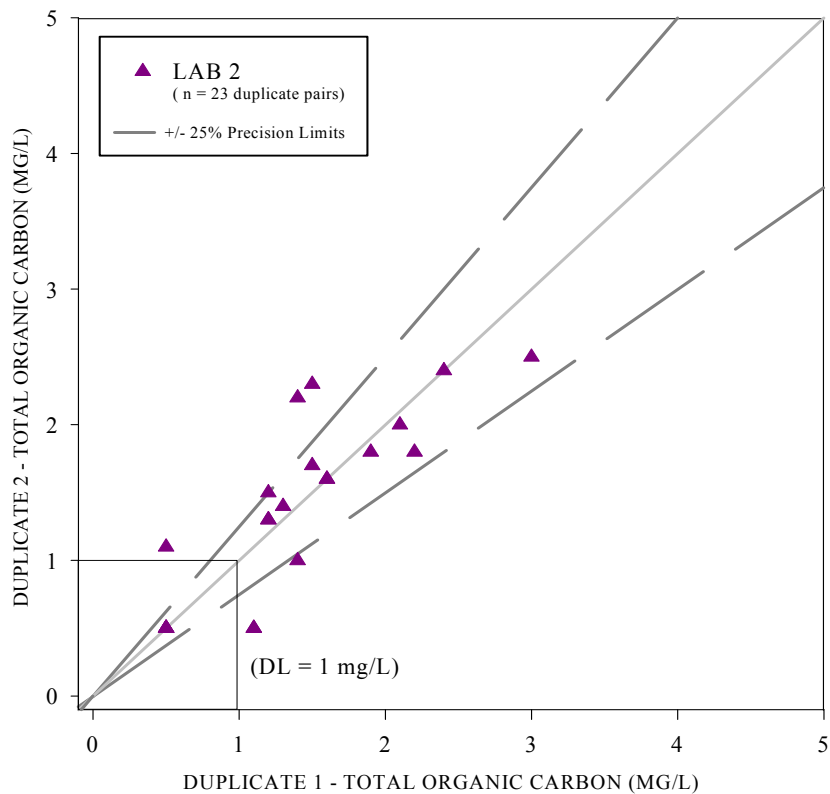


Figure DOC-1. Comparison of Duplicates - Dissolved Organic Carbon - Lab 2 Only

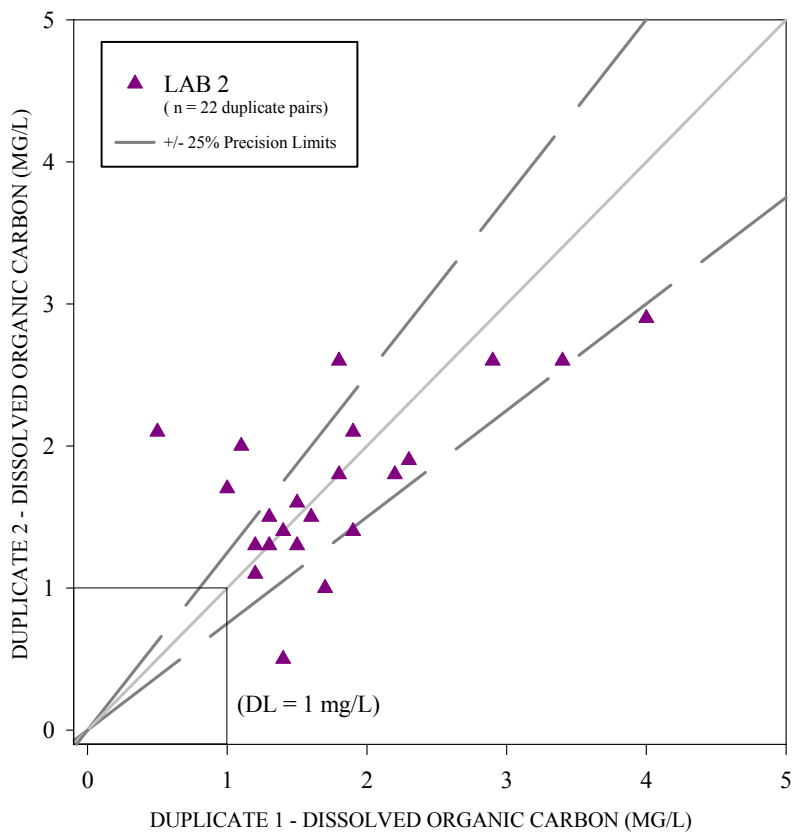


Figure DOC-1 plots the results of duplicate samples for DOC at the second laboratory. It also illustrates the lack of precision in concentrations for the range of values which went to about 4 mg/L. There is no clear indication that MTM/VF mining changes the concentration of TOC or DOC in streams.

5.17.d Total Suspended Solids

Coal mines have specially designed and constructed ditches and sedimentation ponds to reduce erosion and minimize the amount of suspended solids carried from a mine site in surface runoff. Large surface mine operations have elaborate systems required as part of their mining permits. Mine operators regularly monitor and maintain these facilities to capture sediment being washed from their mine site.

There were 213 samples for total suspended solids (TSS) analyzed at the second laboratory and none were rejected in the QA/QC review. A total of 69 of those samples (32 %) had concentrations at or above the detection limit of 5 mg/L. The values were low and this could be due to several factors including: dry fall weather; staff who chose not to sample on rainy days; because the sediment ponds below mined areas were working well; or other unknown causes. Whatever the cause, only 28 samples had a concentration above 10 mg/L. These values were from all categories of sites and are listed below. The data indicate that the concentration of TSS in the streams in the study area was usually below 5 mg/L during the study period.

Site Identification	Category	Concentration (mg/L)
MT-02	Unmined	19
MT-13	Unmined	24
MT-24	Sediment Control Ditch	21, 15, 14, 11
MT-34B	Filled	11
MT-42	Unmined	65, 12
MT-45	Mined	25
MT-48	Filled/Residences	20
MT-52	Filled	53
MT-55	Filled/Residences	51
MT-57B	Filled	11
MT-60	Filled	60, 25, 14
MT-62	Filled/Residences	20, 16
MT-64	Mined/Residences	32, 13, 12
MT-69	Mined/Residences	18
MT-75	Filled/Residences	19, 15
MT-79	Mined	14
MT-86	Filled	27
MT-91	Unmined	21

